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NEW EXCITED STATE VARIATIONAL PRINCIPLES

by



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ABSTRACT

Two new variational principles, of particular interest in obtaining information about excited states, are developed and applied to simple systems.

The first is a variational principle for obtaining upper and lower bounds to eigenvalues of the time independent, non-relativistic Schrödinger equation. It is based on the Temple-Kato formulae and is applied to the H_2^+ ground state and the ground and excited states of the He atom. A comparison is made between this method and a method recently proposed by Löwdin. The methods give very similar results but the present method has the advantage that it can be readily extended to more complex systems.

The second is a variational principle which results in an approximate wave function for the ground or an excited state which has the maximum overlap with the true eigenfunction. The method involves the calculation of $E = \langle \Phi | H | \Phi \rangle$ and $\Delta = \langle \Phi | (H - E)^2 | \Phi \rangle$, but is free of the constraint that the trial function Φ must remain orthogonal to all states of the same symmetry which lie beneath it. One must know, however, an approximation to the true eigenvalue, but a discussion is given on how one might gain the latter information, lacking knowledge of the spectrum, by repeated application of the method.

The method is applied to some excited states of the He atom. It is shown, on the basis of physical properties calculated from the resultant wave functions, that this method is superior to the familiar variational principle used in most quantum chemical calculations. As a result of this, it is hoped that this new method may prove itself to be of particular value in the future in treating problems of chemical interest and determining accurate and tractable wave functions.

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I. General Theory of Upper and Lower Bounds to Eigenvalues

I.1 Introduction

In the application of the Quantum Theory to systems of chemical interest, one is usually attempting to find an approximation, ϕ , to the true wave function, ψ , of the time independent non-relativistic Schrödinger equation. That is, one is trying to solve the equation

$$H\psi = W\psi \quad (1)$$

and determine the energy, W , of a system and the wave function associated with W ; but one must in general compromise with an approximate ϕ and an approximation to W .

For the ground state, the variational principle states that

$$E = \langle \phi | H | \phi \rangle \geq W. \quad (2)$$

This gives an upper bound to the true energy W , but it gives no estimation of the error when the true W is unknown, since there is then no lower bound to the energy. It is of the utmost importance for the prediction of physical phenomena that there exist means to obtain both upper and lower bounds to eigenvalues, not only of the ground state, but also excited states. It is the purpose of this work to 1) investigate various criteria for obtaining upper and lower bounds and to formulate a

method based on a variational principle for the determination of these bounds, and 2) develop a new variational principle for excited states.

In section I.2 the formulae which have been proposed to determine an upper or lower bound from a knowledge of a variationally determined approximate wave function ϕ_k will be reviewed.

This will lead in section I.3 to the question: what is the ϕ which serves as the best approximation to Ψ ? After reviewing criteria for the quality of a trial function, a method will be given to obtain the best ϕ_k , i.e., the best approximation to Ψ_k .

After having obtained a method for determining the best ϕ_k , in section I.4, the question of the best bounds is taken up. It is discovered that the combination of the best ϕ_k determined variationally by the approach given in section I.3 when combined with the bound formulae discussed in section I.2 does not give the best upper and lower bounds. A method is then presented to obtain the best bounds. It is noted there that the formulae for the best bounds and the formula for the best ϕ_k , discussed in section I.3, have the same form.

In section I.5 consideration of the work in the literature is given. It is shown that the methods of sections I.3 and I.4 provide a good basis for an analysis of the work in the literature. Also the literature

supports the contentions made in sections I.3 and I.4.

In section I.6 alternative methods to the calculation of lower bounds are considered. All of the work considered in sections I.2 - I.5, and indeed all the work which is presented in Chapters II and III, are based on a variational principle. In section I.6, however, methods based on a perturbation approach are outlined for completeness.

I.2 Formulae for Bounds

The first mention in the literature of a method for determining a lower bound to eigenvalues is in the work of G. Temple (1). He proposed that, for the ground state, one should obtain a lower bound by applying the formula

$$B = E + \frac{\Delta}{E - \gamma} \quad (3)$$

where B is the lower bound and

$$E = \langle \phi | H | \phi \rangle, \quad \Delta = \langle \phi | (H - E)^2 | \phi \rangle \quad (4)$$

and where γ is an approximation to the eigenvalue of the first excited state. ϕ is an approximate eigenfunction which satisfies Eq. (2). Thus Eq. (2) gives an upper bound and Eq. (3) a lower bound to the exact eigenvalue.

Later D. H. Weinstein (2) proposed another method

for lower bounds which could also be used for excited states. According to Weinstein there is some energy level W_k which satisfies the relation

$$E + \sqrt{\Delta} \geq W_k \geq E - \sqrt{\Delta} \quad (5)$$

where E and Δ are as defined in Eq. (4). Δ may also be written as

$$\Delta = D - E^2, \text{ where } D = \langle H\Phi | H\Phi \rangle \quad (6)$$

If Φ is expanded in the complete set of eigenfunctions ψ_i , then

$$\Phi = \sum_n a_n \psi_n \quad (7)$$

and thus

$$E = \sum_n a_n^* a_n W_n, \quad D = \sum_n a_n^* a_n W_n^2 \text{ and } \sum_n a_n^* a_n = 1. \quad (8)$$

In what follows it will be assumed that Φ is a real function and hence $a_n^* a_n$ will be written as a_n^2 . From Eqs. (6) and (8) one obtains

$$\Delta = D - E^2 = \sum_n a_n^2 W_n^2 - 2E \sum_n a_n^2 W_n + E^2 \sum_n a_n^2 = \sum_n a_n^2 (W_n - E)^2 \quad (9)$$

The argument then is that there is some energy level W_k which is at least as near as any other, i.e., for which

$$(W_k - E)^2 \leq (W_n - E)^2 \quad (10)$$

Hence

$$\Delta \geq (W_k - E)^2 \sum_n a_n^2 \text{ or } \Delta \geq (W_k - E)^2. \quad (11)$$

There are now two cases to consider:

$$W_k \geq E \quad \text{and} \quad W_k < E.$$

In the first case

$$\sqrt{\Delta} \geq W_k - E \quad \text{and thus} \quad E + \sqrt{\Delta} \geq W_k \geq E \quad (12)$$

and in the second

$$\sqrt{\Delta} \geq E - W_k \quad \text{and} \quad E > W_k \geq E - \sqrt{\Delta}. \quad (13)$$

Combining Eqs. (12) and (13), Weinstein's statement, Eq. (5), is obtained. This method however has some undesirable characteristics which will be pointed out later.

Several other methods for calculating lower bounds based on the use of Δ and E were proposed, but the work of Kato (3), placed all of them on a common basis. Indeed, he showed that the Temple formula was the best lower bound which could be obtained with a knowledge of Δ , E and an approximation to the energy of the first excited state. He moreover extended the method to excited states, to yield upper bounds as well as lower bounds. Kato's theorem will now be stated.

Kato's Theorem: If it is assumed that the interval $(\tilde{E}_{i-1}, \tilde{E}_{i+1})$ contains no point of the spectrum other than a non-degenerate eigenvalue, and that, for a trial function ϕ , E and Δ are calculated and satisfy the inequality

$$\Delta < (E - \tilde{E}_{i-1})(\tilde{E}_{i+1} - E) \quad (14)$$

then the interval certainly contains one and only one eigenvalue W_i such that

$$E + \frac{\Delta}{E - \tilde{E}_{i+1}} = B^L \leq W_i \leq B^U = E + \frac{\Delta}{E - \tilde{E}_{i-1}}. \quad (15)$$

In general Eq. (15) cannot be replaced by a more precise formula if only the quantities E , Δ , \tilde{E}_{i-1} and \tilde{E}_{i+1} are known, whatever these quantities may be. The proof is as follows:

One may write the Hamiltonian in terms of its eigenvalues and eigenfunctions as

$$H = \sum_i W_i \psi_i \psi_i^* \quad (16)$$

where it is assumed here, for simplicity, that the spectrum is entirely discrete.

It is assumed that for a normalized vector ϕ in the domain of H the following quantities are calculated

$$\langle \phi | H | \phi \rangle = E, \quad \langle \phi | (H - E)^2 | \phi \rangle = \Delta. \quad (17)$$

Lemma 1: For every \tilde{E}_{i-1} such that $\tilde{E}_{i-1} < E$ ($\tilde{E}_{i-1} \rightarrow -\infty$ is permitted), the interval $(\tilde{E}_{i-1}, B^U]$ contains a point of the spectrum, where B^U is defined by

$$B^U = E + \frac{\Delta}{E - \tilde{E}_{i-1}}. \quad (18)$$

Proof of Lemma 1: If the interval (\tilde{E}_{i-1}, μ) for $\mu > \tilde{E}_{i-1}$, contains no point of the spectrum, the quadratic expression

$$(E - \tilde{E}_{i-1})(E - \mu) = E^2 - (\tilde{E}_{i-1} + \mu)E + \tilde{E}_{i-1} \mu \quad (19)$$

cannot take on a negative value as E varies over the spectrum. The same will be true if E is replaced by W_i and then Eq. (19) is multiplied by $\langle \Phi | \Psi_i \rangle \langle \Psi_i | \Phi \rangle$, and this expression is summed over i . Since

$$\sum_i \langle \Phi | \Psi_i \rangle W_i^2 \langle \Psi_i | \Phi \rangle = \langle \Phi | H^2 | \Phi \rangle = \Delta + E^2 \quad (20)$$

and

$$\sum_i \langle \Phi | \Psi_i \rangle W_i \langle \Psi_i | \Phi \rangle = E \quad (21)$$

it follows that

$$\Delta + E^2 - (\tilde{E}_{i-1} + \mu)E + \tilde{E}_{i-1} \mu \geq 0 \quad (22)$$

or

$$\mu \leq E + \frac{\Delta}{E - \tilde{E}_{i-1}} = B^u. \quad (23)$$

This means that the interval (\tilde{E}_{i-1}, μ) contains a point of the spectrum if $\mu > B^u$, and since the spectrum is a closed set, the same is true of the interval $(\tilde{E}_{i-1}, B^u]$.

Lemma 2: For every \tilde{E}_{i+1} such that $\tilde{E}_{i+1} > E$, the interval $[B^l, \tilde{E}_{i+1})$ contains a point of the spectrum, where B^l is defined by

$$B^l = E + \frac{\Delta}{E - \tilde{E}_{i+1}}. \quad (24)$$

This proof follows the one given for Lemma 1. Now, combining the two lemmas, it is clear that each of the intervals $(\tilde{E}_{i-1}, B^u]$ and $[B^l, \tilde{E}_{i+1})$ contains a point of the spectrum. Since equation (14) really means that $B^u < \tilde{E}_{i+1}$ and $B^l > \tilde{E}_{i-1}$, it must be concluded that $[B^l, B^u]$ contains a point of the spectrum, W_i .

In the above theorem B^l and B^u are the lower and upper bounds respectively, and the \tilde{E}_γ are approximations to the eigenvalues of the γ^{th} state.

Hereafter we will consider in detail only Weinstein's method and Temple's method as extended by Kato as a means of calculating bounds, since the former gives the best bound obtainable with the information E and Δ , and the latter gives the best bound obtainable from E , Δ and E_γ . There are other methods, which will be mentioned briefly later, which give lower bounds without the knowledge of Δ . These methods avoid the calculation of Δ , which involves quite difficult integrals, but introduce complications of their own.

It should be noted that the formulae which will be considered, namely Eqs. (5) and (15), assume that one knows an approximate wave function to the k^{th} state, ϕ_k , in order to obtain a bound to the eigenvalue of that state. This obviously presents the problem of determining such an approximate wave function for the k^{th} state. This problem will now be considered in detail.

1.3 Determination of ϕ_k .

For the exact wave function ψ of an eigenstate the following equations hold,

$$E = \langle \psi | H | \psi \rangle = W \quad (25)$$

$$\Delta = \langle \psi | H^2 - E^2 | \psi \rangle = 0 \quad (26)$$

and if ψ is an eigenstate with $E \neq E'$, where E' is the energy of another state of the same symmetry with the corresponding eigenfunction ψ' , then

$$\langle \psi | \psi' \rangle = 0. \quad (27)$$

For a trial function ϕ , one has $E = \langle \phi | H | \phi \rangle > W_0$, where W_0 is the true ground state energy. Indeed if ϕ were capable of attaining the exact form of ψ_0 , the exact ground state eigenfunction, one would have $E = W_0 = \langle \psi_0 | H | \psi_0 \rangle$.

Likewise for a calculation of an excited state, if the trial function ϕ is capable of attaining the form of ψ_k under a variation, then a stationary state is obtained with $E = W_k = \langle \psi_k | H | \psi_k \rangle$. In both cases it is to be noted that the true eigenvalues are obtained by finding the stationary value from $\delta E = 0$ for the case of a trial function which can become the eigenfunction under variation.

For an excited state ψ_k of the same symmetry as the

ground state ψ_0 , $\delta E = \delta \langle \phi | H | \phi \rangle = 0$ is a necessary condition for finding a stationary value E which approximates W_k ; but it is not sufficient. One must also take account of Eq. (27). Thus with Eqs. (25) and (27) using ϕ in place of ψ one has necessary and sufficient conditions so that $\phi \rightarrow \psi_k$: $\delta \langle \phi | H | \phi \rangle = 0$ and $\langle \phi | \phi_0 \rangle = 0$. But the condition $\langle \phi | \phi_0 \rangle = 0$ is rather restrictive, especially if ϕ_0 is not a very good approximation to ψ_0 . Hence it is desirable to find another approach for excited states.

Now Weinstein (2) has proposed that for an excited state for which one has a trial function ϕ , which cannot obtain the form of an exact wave function, one can obtain an approximation to some ψ_k by minimizing Δ , where Δ is given by Eq. (4).

A simple theorem states that: if there exists a ϕ such that $H\phi = W_k \phi$ (hence $\phi = \psi_k$), then $\Delta = 0$. As a corollary it may be stated that as $\phi \rightarrow \psi_k$, $\Delta \rightarrow 0$. Hence $\phi \rightarrow \psi_k$ implies that $\Delta \rightarrow 0$. It is on this basis that Weinstein suggested that as $\Delta \rightarrow \min.$, $\phi \rightarrow \psi_k$. It will be shown below that if one measures the approach of ϕ to ψ_k by the increase of the value of the integral $a_k = \langle \phi | \psi_k \rangle$, the minimization of Δ does not at all give the best approximation to a ψ_k that can be obtained from a given trial function.

There are criteria for judging the goodness of ϕ as an approximation to ψ_k other than that of the

maximum a_k , but a_k provides for the best overall convergence of ϕ to ψ_k . Obtaining the maximum a_k is equivalent to obtaining the smallest root-mean-square deviation of ϕ from ψ_k . As will be seen below, the other criteria are useful for obtaining good approximations to ψ_k in certain regions of configuration space, but since a_k provides a criterion for judging the goodness of ϕ as an approximation to ψ_k over the entire configuration space, it seems that this criterion should be the one used to judge the goodness of ϕ .

Criteria of Goodness for Approximate Wave Functions

In this section, a generalization is presented of an analysis first given by H. M. James and A. S. Coolidge (4) for the ground state of an electronic system. Here the method will be extended to apply to excited states as well.

Let ϕ be an approximate normalized wave function and $E = \langle \phi | H | \phi \rangle$ its associated energy. Also let

$$\phi = \sum_i a_i \psi_i = \sum_{i \neq k} a_i \psi_i + a_k \psi_k. \quad (28)$$

Now

$$(\phi - a_k \psi_k) = \sum_{i \neq k} a_i \psi_i \quad (29)$$

will give the deviation of ϕ from the exact function ψ_k . A deviation function can then be defined,

$$\phi_x = (1 - a_k^2)^{-\frac{1}{2}} (\phi - a_k \psi_k) \quad (30)$$

where $a_k = \langle \psi_k | \phi \rangle$. Hence one may write

$$\phi = a_k \psi_k + a_x \phi_x \quad (31)$$

where $a_x = (1 - a_k^2)^{\frac{1}{2}}$ measures the amount of the deviation function ϕ_x which appears in ϕ . As criteria of the inaccuracy of ϕ there are: Q , the root-mean-square error in ϕ

$$Q = \langle \phi - \psi_k | \phi - \psi_k \rangle^{\frac{1}{2}} \quad (32)$$

ϵ , the energy error

$$\epsilon = |E - W_k| \quad (33)$$

and $\Delta^{\frac{1}{2}}$, the root-mean-square local energy deviation

$$\Delta^{\frac{1}{2}} = \langle \phi | (H - E)^2 | \phi \rangle^{\frac{1}{2}}. \quad (34)$$

One may also define the quantities

$$E_x = \langle \phi_x | H | \phi_x \rangle, \quad \epsilon_x = |E_x - W_k|$$

and

$$\Delta_x = \langle \phi_x | (H - E)^2 | \phi_x \rangle. \quad (35)$$

If the inequality

$$\langle \phi_x | [(H - E) - (E_x - E)]^2 | \phi_x \rangle \geq 0$$

is considered, and the integral is expanded in terms of the above defined quantities, one finds

$$\langle \phi_X | H^2 | \phi_X \rangle - 2E_X E + E^2 - E_X^2 + 2E_X E - E^2 \geq 0.$$

Thus,

$$\langle \phi_X | H^2 | \phi_X \rangle - 2E_X E + E^2 \geq E_X^2 - 2E_X E + E^2.$$

But the left hand side is merely Δ_X , hence

$$\Delta_X \geq (E_X - E)^2. \quad (36)$$

From the definitions of ϵ_X and ϵ given above, it can be shown that $(E_X - E)^2 = (\epsilon_X - \epsilon)^2$, hence $\Delta_X \geq (\epsilon_X - \epsilon)^2$.

Thus one may define a quantity K^2 ,

$$K^2 = \frac{\Delta_X}{(\epsilon_X - \epsilon)^2} \geq 1. \quad (37)$$

Now substituting Eq. (31) into Eqs. (32) - (34), it follows that

$$Q^2 = 2[1 - a_k] = 2[1 - (1 - a_X^2)^{\frac{1}{2}}] \quad (38)$$

$$\epsilon = a_X^2 \epsilon_X \quad (39)$$

$$\Delta = \epsilon^2 + a_X^2 (\Delta_X - \epsilon^2). \quad (40)$$

From the first equality of Eq. (38) one finds the justification of the statement made in the last section, that obtaining the maximum a_k is equivalent to obtaining the smallest root-mean-square deviation.

Eliminating a_X between Eqs. (38) and (39) one finds

$$Q^2 - \frac{1}{4} Q^4 = a_X^2 = \epsilon / \epsilon_X \quad (41)$$

or if ϕ is a fairly good approximation to ψ_k (i.e., if ϵ is small when compared to $|W_k - W_{k-1}|$ and $|W_k - W_{k+1}|$), then

$$Q^2 \approx \epsilon / \epsilon_x. \quad (42)$$

Eliminating a_x between Eqs. (39) and (40) one obtains

$$\Delta = \epsilon [\epsilon + (\Delta_x - \epsilon^2) / \epsilon_x] \quad (43)$$

and assuming again that ϕ is a fairly good approximation to ψ_k , it follows that

$$\Delta / \Delta_x \approx \epsilon / \epsilon_x \quad \text{or} \quad \Delta \approx \epsilon \epsilon_x K^2. \quad (44)$$

Now, making use of Eqs. (42) and (44), one obtains the result

$$Q^2 \approx \left(\frac{\epsilon^2}{\Delta} \right) K^2. \quad (45)$$

This equation interrelates the various criteria considered. Again it should be emphasized that theoretically the criterion which should be used to judge the overall quality of a wave function is the criterion of minimum Q^2 (i.e., maximum a_k).

Before proceeding to investigate Eq. (45), each of the quantities in this equation must be studied in order to understand its consequences and enable one to proceed to a method for determining the best ϕ to approximate ψ_k .

Assume first that one has a function ϕ . One may then, according to Eqs. (32) - (34), judge its accuracy.

It should be noted that in applying these formulae directly that Eq. (32) requires a knowledge of the true wave function. This is not available, of course, except for the very simplest systems; thus Eq. (32) is impractical from this point of view.

In order to use Eq. (33) one must know the true eigenvalue W_k ; however, for this quantity the experimentally determined energy for this state may be used, if it has been measured. Thus this method of judging accuracy usually will be available.

Finally, it should be noted that Eq. (34) makes no use of information other than that contained in ϕ . Although this seems to be a favorable aspect of Eq. (34) it must be realized that one is only finding the local energy deviation on the basis of ϕ without regard to any external standard.

The three criteria have now been considered assuming that a ϕ had somehow been obtained. A more important question is whether the criteria can be used to determine a ϕ . This is obviously the only way one can obtain a ϕ which approximates a ψ_k , because if one does not have criteria to guide one in obtaining a ϕ , how then does one obtain such a function?

From this point of view Eq. (32) is useless; because if ψ_k is known, why should one want to obtain an approximation to it? Eq. (33) can be used to obtain a ϕ , if one

assumes that ϕ is the function which minimizes ϵ . That is, a ϕ must be found such that $\delta\epsilon = 0$. For the ground state this is nothing more than the familiar variational principle. Eq. (33) is, however, incapable of giving a ϕ which is an approximation to an excited state which has the same symmetry as the ground state.

Considering Eq. (34) one must find the ϕ which minimizes Δ . It is the only one of the criteria which, taken alone, can yield a ϕ for the ground state or any excited state. It is for this reason that it has been suggested by Weinstein as a method for determining approximations to ψ_k . Referring again to Eq. (45) however, it is obvious that Weinstein's idea of minimizing Δ does not give the minimum Q^2 and thus this method cannot give the best overall approximation to ψ_k . But looking at each of the three criteria individually and demanding that Q^2 be a minimum, an impasse seems to be reached. It will be shown shortly that this impasse is resolved by Eq. (45). But first brief consideration will be given to the types of error in the wave function which are reduced by minimization of Δ and the minimization of E ; here the discussion given by James and Coolidge (4) is important.

In minimizing Δ , the "local energy error" is minimized (4, 5). That is, the errors in the wave function associated with the closeness of the electrons will be minimized. Thus the wave function which results from this type of

minimization would be expected to give good values for properties which describe phenomena where the particles are close together.

In minimizing E , which can be done only for the ground state or lowest state of a given symmetry, "long range errors" are minimized (4, 5, 6). Thus a wave function determined on this basis should be good for describing properties such as the radial density or diamagnetic susceptibility where long range errors are important. Thus by minimizing E or Δ , a wave function is obtained which has minimum error in certain regions of configuration space, rather than the minimum error over the whole of configuration space.

Now returning to Eq. (45) one may ask how one might obtain a wave function for an excited state which satisfies the criteria of minimum Q^2 . From the derivation of Eq. (45) it was found that $K^2 \geq 1$, according to Eq. (37). Thus, if the right hand side of Eq. (45) is to be minimized, the smallest value K^2 can take is 1. Thus, in order to obtain the minimum Q^2 , the quantity ϵ^2/Δ should be minimized. This method allows the determination of an excited state wave function which minimizes Q^2 without a knowledge of the exact ψ_k . This seems to be the first time that this procedure has been proposed as a method for obtaining approximations to excited state wave functions.

On the basis of the new method just proposed above, it is now known how to obtain a ϕ which is the best approximation to a ψ_k . It should be noted that the ϕ_k obtained by this method for the case of a ground state need not give as good an approximation to W_0 as could be obtained by minimizing E ; likewise, it need not give as small a value for Δ as would be obtained by minimizing Δ . However, unlike the minimization of Δ or E , it does give the minimum Q^2 which is the chosen criterion for the best ϕ_k .

I.4 The Determination of the Best Bounds

In the last section it was found that one can obtain the best ϕ_k by minimizing ϵ^2/Δ . Hence with this wave function one may return to the formulae of section I.2 for upper and lower bounds. In particular one is interested in Eqs. (5) and (15). If ϕ_k is substituted into Eq. (15) along with the \tilde{E}_γ , the best bounds to the k^{th} state will be obtained that ϕ_k can give. If there is no knowledge of the \tilde{E}_γ , then one must settle for the bounds from Eq. (5).

Thus the best bounds available for the function ϕ_k have been obtained. But, have the best bounds to the k^{th} state which can be obtained from the form of the trial function ϕ been determined? The answer is no, not necessarily. In the last section it was found that

the best function judged by Δ minimization is not the same as the best function as obtained by ϵ minimization of ϵ^2/Δ ; similarly the bounds based on ϕ_k , obtained by Eq. (45), may not be as good as the ones based on another method. The method to be used to determine these better bounds will be outlined now.

First, consider Eq. (5); for the lower bound one has

$$B^L = E - \sqrt{\Delta} \quad (46)$$

and for the upper bound

$$B^U = E + \sqrt{\Delta} . \quad (47)$$

If one wishes to obtain the best bounds which can be given by a function of the form ϕ , one should maximize Eq. (46) with respect to ϕ and obtain a $\phi^{\max.}$ and then minimize Eq. (47) with respect to ϕ and thus obtain a $\phi^{\min.}$. If $\phi^{\max.}$ and $\phi^{\min.}$ are determined with regard to the k^{th} state they may be labeled as $\phi_k^{\max.}$ and $\phi_k^{\min.}$. The relationship which exists between $\phi_k^{\max.}$, $\phi_k^{\min.}$ and ϕ_k is at best obscure. Thus it seems that one is given the choice of obtaining the best ϕ_k and calculating bounds from it which will not necessarily be the best bounds, or calculating the best bounds and obtaining thereby $\phi_k^{\max.}$ and $\phi_k^{\min.}$ which may not necessarily be good approximations to ψ_k .

At this point the choice of trying to determine the best bounds to a given state will be made, rather

than trying to determine the best ϕ_k . What is clear from the preceding discussion is that the method proposed by Weinstein, i.e., the minimization of Δ , yields neither the best ϕ_k nor the best bounds. This point will be returned to again later.

Having chosen this course, it is necessary now to consider the Temple-Kato formula, Eq. (15). Here, as with the Weinstein formula considered above, one wishes to maximize the lower bound and minimize the upper bound. Hence one again will obtain a $\phi_k^{\max.}$ and a $\phi_k^{\min.}$.

With Eq. (15), if a maximum and minimum can be found at all, it will be guaranteed by Kato's theorem that the corresponding bounds B^{ℓ} and B^u will be bounds to the k^{th} state which is under consideration. This is in contrast to the method based on the maximization of Eq. (46) and the minimization of Eq. (47). For although one will obtain in this manner the best B^{ℓ} and B^u obtainable from Weinstein's formula, one is not insured that they will be the best bounds to the state under consideration; they may in fact be the best bounds to an entirely different state. In order to get the best bounds to the desired state, one must make a very judicious choice of the trial function ϕ . This is one inconvenience of a theory based on the Weinstein formula.

It is to be noted that the bounds obtained from maximizing B^{ℓ} and minimizing B^u as given by Eq. (15) are

in any event always better than those obtained from maximizing Eq. (46) and minimizing Eq. (47), (3). Of course in operating with Eq. (15) one must always have a knowledge of the \tilde{E}_γ .

It is now proposed that the method outlined above, which is based on Eq. (15), will determine the best bounds which can be obtained from a knowledge of E and Δ . Now proceeding from the outline given above, this new proposal will be considered in detail.

Rewriting Eq. (15) in the following form

$$B = E + \frac{\Delta}{E - \tilde{E}_\gamma} \quad (48)$$

where B is an upper or lower bound depending upon whether γ is $k - 1$ or $k + 1$, and demanding the variation in B should vanish for the bounds, the following is obtained

$$\delta B = 0 = \delta E + \frac{\delta \Delta}{E - \tilde{E}_\gamma} - \frac{\Delta \delta E}{(E - \tilde{E}_\gamma)^2} \quad (49)$$

This may be rewritten as

$$\delta B = \delta E + \left[\frac{(E - \tilde{E}_\gamma)}{(E - \tilde{E}_\gamma)^2 - \Delta} \right] \delta \Delta = 0 \quad (50)$$

which states that the trial function ϕ which makes the variation in B vanish will serve as the function to obtain the best bound when it is used in Eq. (48).

In particular, it is assumed that one is interested in obtaining upper and lower bounds to the eigenvalue of

the k^{th} state. For the upper bound of the k^{th} state one would need \tilde{E}_{k-1} , an approximation to the eigenvalue of the $(k-1)^{\text{th}}$ state. With \tilde{E}_{k-1} and a ϕ , one would use Eq. (50) to determine the $\phi_k^{\text{min.}}$, which gives the best upper bound to W_k . The ϕ which satisfies Eq. (50) in this case, $\phi_k^{\text{min.}}$, must be such as to yield the minimum value of Eq. (48).

For the lower bound one would use \tilde{E}_{k+1} and determine by use of Eq. (50) the $\phi_k^{\text{max.}}$ which would yield the best lower bound. This function would yield the best lower bound obtainable from a function of type ϕ , when it was substituted into Eq. (48).

Thus, so long as one knows an \tilde{E}_{k+1} and an \tilde{E}_{k-1} , one is insured by Kato's theorem that when Eq. (50) is used one will determine bounds to the k^{th} state; Eq. (50) also guarantees that the bounds are the best obtainable from a function of the form ϕ . It should be noted that from Kato's theorem the inequality $\Delta < (E - \tilde{E}_{k-1})(\tilde{E}_{k+1} - E)$ must be satisfied. This does not however imply that Δ must bracket W_k , i.e., $E - \sqrt{\Delta} \leq W_k \leq E + \sqrt{\Delta}$, as seems to have been assumed in the literature in the past (7, 8, 9). On the contrary Δ as determined by a $\phi_k^{\text{max.}}$ may be such that $E - \sqrt{\Delta} \leq W_{k+1} \leq E + \sqrt{\Delta}$, and yet this Δ and $\phi_k^{\text{max.}}$ will serve to give a lower bound to the k^{th} state. The only restriction on Δ is that it must satisfy the inequality

Eq. (14), in Kato's theorem.

Now Eqs. (46) and (47) may be written as

$$B = E \pm \sqrt{\Delta} \quad (51)$$

where B is an upper or lower bound depending upon whether the plus or minus sign is chosen. There is an interesting relationship among Eqs. (45), (48) and (51) which is worthwhile developing.

Considering Eq. (51) first, if the variation in B is set to zero one obtains

$$\delta B = \delta E + \left[\frac{\pm 1}{2\sqrt{\Delta}} \right] \delta \Delta = 0 \quad (52)$$

This equation is to be interpreted in the same manner as Eq. (50); note also the similarity of the two equations. They differ only in the coefficient of $\delta \Delta$.

Now, considering Eq. (45), the variation in Q^2 should vanish. Hence one writes, considering the arguments put forward before on the minimization of Q^2 ,

$$\delta Q^2 = \delta E - \left[\frac{|W_k - E|}{2\Delta} \right] \delta \Delta = 0 \quad (53)$$

which has the same form as Eqs. (52) and (50). The only difference is again the coefficient of $\delta \Delta$. Thus one may write all three of these equations in the common form

$$\delta E + \omega \delta \Delta = 0 \quad (54)$$

where the coefficient ω depends upon whether one wants

- a) the best bounds obtainable from a ϕ with knowledge of E and Δ and \tilde{E}_γ , Eq. (50)
- b) the best bounds available from a ϕ with a knowledge of only E and Δ , Eq. (52)
- c) the best wave function ϕ_k obtainable with the knowledge of only W_k , Eq. (53).

Thus all of the methods which have been developed can be summarized by Eq. (54). Whether there is any deeper significance to the fact that these three methods can be represented by a common form is at the moment not clear. But it should certainly be interesting to pursue this line of thought further.

Before leaving this section on the determination of the best bounds it may be of profit to mention a drawback in the use of Eqs. (48) and (50), since these are the equations which will be used to develop a working scheme, based on orbital theory, in the next chapter. The drawback, of course, is that one has to know the \tilde{E}_γ . The better they are known, the better the bounds will be. The best values are, of course, $\tilde{E}_{k+1} = W_{k+1}$ and $\tilde{E}_{k-1} = W_{k-1}$, and thus, if there is experimental information available, it could be used for the \tilde{E}_γ . However, it may be that no experimental information is available in a particular case; how then could one obtain the \tilde{E}_γ ?

The \tilde{E}_γ could perhaps be determined a priori in the

following way. Suppose, for a definite example, that one wishes to determine the upper and lower bounds of the second excited state of a given symmetry and has no information about the spectrum of eigenvalues. Thus, with no experimental data, one must calculate everything a priori.

One would first of all be able to obtain $E_0 = B_0^u$, that is the upper bound to the ground state, by means of the familiar variational principle. Now for the first excited state one would use $B_0^u = E_0$ as \tilde{E}_0 in Eqs. (50) and (48) and thus be able to obtain a B_1^u , which represents an upper bound to the first excited state. To determine the upper bound to the second state one would now use B_1^u as \tilde{E}_1 and proceed as before to obtain B_2^u . In order to obtain a lower bound to W_2 , one must first of all calculate an upper bound to W_3 , B_3^u , in the same manner as for B_1^u and B_2^u . Now with B_3^u as \tilde{E}_3 Eqs. (50) and (48) may be used to obtain a lower bound, B_2^l , to W_2 . Care must be exercised in this last step however, for B_3^u is of necessity above W_3 , thus two true eigenvalues will be found between B_3^u and B_1^u . This, however, violates the conditions necessary for Kato's theorem to be true. Thus one would have to use a value slightly less than B_3^u in order to avoid this difficulty. The inequality, $\Delta < (E - \tilde{E}_{i-1})(\tilde{E}_{i+1} - E)$, should aid greatly in detecting problems like the one just mentioned. For since B_3^u

is above W_3 , the calculation should try to find a B_3^{ℓ} which would give an E above W_3 . But in this case when the proper quantities are substituted into the inequality a positive quantity on the left side and a negative quantity on the right side would result. Hence one would know that something was wrong and thus decrease the value of B_3^u . This is a very simple scheme presented here; more elaborate and accurate ones certainly could be imagined. Perhaps in the future it would be worth while to investigate in detail such possible alternatives, and thus be freed from using experimental data in the calculations.

I.5 Considerations of Previous Work

There have been few applications of either Weinstein's or Temple's formula in the literature, mostly due to the difficulty of evaluating the integrals in Δ . The few applications which have appeared (7, 9, 10, 11), have been mainly to the ground states of He and H_2^+ . In these cases the ϕ which is used to calculate the lower bound is calculated by means of the variational principle, i.e., minimization of E ; in Goodisman's work on H_2^+ , the minimization of Δ is used. In the cases where E is minimized the lower bounds are poor, but according to the analysis of the last section this is to be expected. For if ϕ is obtained with the criterion of the minimum

E , then Δ will increase and since Δ or its square root appear in the numerator of both formulae this will increase the quantity which is added to E in both cases. This will make the bound worse. In the case of Δ minimization, E increases and thus the lower bound should be better than in the case of E minimization. However neither minimization will give a better bound than the procedure for best bounds which was described in the last section. An illustration of this will be given in Chapter III for the case of H_2^+ .

There seems to be some confusion in the literature on bounds. For instance, in a paper by Fröman and Hall (7), one finds the statement that for a particular approximate function ϕ_I for the ground state of He the Weinstein formula gives a better lower bound than the Temple formula. This, of course, is incorrect; the Weinstein formula can never give a better bound than the Temple equation, as was shown by Kato (3). If one examines Table I in their paper it is readily apparent that their values of $E - \sqrt{\Delta}$ and $E + \sqrt{\Delta}$ bracket two eigenvalues. This contradicts Weinstein's initial assumption, Eq. (5), and hence Fröman and Hall's observation about ϕ_I is entirely invalid.

Goodisman (12) claims to have derived a new method for obtaining upper bounds to excited states. Starting from a consideration of Stevenson's formula (13) for

lower bounds, which is poorer than Temple's equation, he obtains a formula for upper bounds, which, however, is a special case of the Temple-Kato formula, Eq. (15). It cannot give as good a bound as Eq. (15), (3).

In a recent publication, Goodisman (5) considers the minimization of E and Δ as criteria for obtaining a good approximation to the ground state eigenfunction of the H_2 system. He considered the variational function of Kolos and Wolniewicz (14) to represent the exact function closely and used James and Coolidge type functions of varying complexity as trial functions ϕ_i . Then after obtaining the parameters in the ϕ_i by either minimization of E or minimization of Δ he compared the resulting ϕ_i to the Kolos and Wolniewicz function by calculating the overlap between the two functions. On the basis of maximum overlap he then was able to come to conclusions about the goodness of the approximate functions. His results showed that minimizing Δ did not give a larger overlap with the "true" function than minimizing E .

Kolos and Roothaan (15) and Kolos and Wolniewicz (14) also calculated a number of expectation values of properties with their function for H_2 . Goodisman chose to calculate $\langle H \rangle$, $\langle 3z^2 - r^2 \rangle$, $\langle 1/r_{12} \rangle$ and $\langle \delta \vec{r}_{12} \rangle$ for his trial functions, which were obtained by both minimization of E and minimization of Δ and compare them to the "true" values obtained

by Kolos et. al. $\langle H \rangle$ is the total electronic energy, $\langle 3z^2 - r^2 \rangle$ is the electronic contribution to the quadrupole moment, $\langle 1/r_{12} \rangle$ is the interelectronic repulsion energy and $\langle \delta \vec{r}_{12} \rangle$ represents the size of the set of points where two electrons are coincident. The latter term arises in the relativistic correction to the energy. $\langle 1/r_{12} \rangle$ and $\langle \delta \vec{r}_{12} \rangle$ should be particularly sensitive to local fluctuations of the wave function; hence one would suspect that they might be better calculated with a Φ obtained from Δ minimization. However, the conclusion from the data presented is that the expectation values calculated using the functions obtained by the minimization of E are closer to the correct values than those obtained by minimization of Δ . The exception is $\langle \delta \vec{r}_{12} \rangle$ which is certainly a "very short range" property and highly sensitive to local energy errors. It is a bit discouraging however, that $\langle 1/r_{12} \rangle$, which should be sensitive to local energy errors, is better determined by the E than by the Δ minimized Φ . Goodisman's results here definitely support the analysis given in section I.3, and support the contention that Δ minimization does not seem to be a good method to determine approximate wave functions.

A general method for obtaining a Φ , within the orbital approximation, by minimization of Δ , has been proposed by Fraga and Birss (16); since the method is

based on the minimization of Δ , it has the theoretical disadvantages pointed out already. Their actual procedure is very useful however and much of their work can be used to formulate a more general procedure based on the arguments presented in section I.4. It will be shown in the next chapter that, using their basic approach of determining pseudo-eigenvalue equations by means of coupling operators from a general variational principle and combining this with Eq. (54), one is able to develop equations which give a unified approach to both the best bounds and the best wave function. These equations, which will determine the best bounds or the best wave function, will be identical in form and will differ only by the constant ω which will appear in the general coupling operators.

All of the work discussed so far and indeed also the method which we will develop in the next chapter are based on some sort of variational procedure. There are also methods based on perturbation theory for the determination of lower bounds but these methods are not capable of giving upper bounds; thus the upper bounds must be determined by another method. These methods will be briefly discussed in the next section.

I.6 Other Methods of Determining Lower Bounds

The first method of determining lower bounds which

will be considered is based on the so-called method of intermediate Hamiltonians. The approach of Bazley (17) is followed here.

The method consists of writing the total Hamiltonian as a sum of two parts

$$H = H^0 + H'. \quad (55)$$

The first part must have a simple enough form so that the Schrödinger equation involving it may be solved exactly. The second term, H' , must be a positive definite operator, i.e., $\langle \phi | H' | \phi \rangle > 0$ must hold for all ϕ in the domain of H' . The eigenvalue problem for H^0 is known as the base problem and, if W_i^0 are the eigenvalues of H^0 , they will give rough lower bounds to the eigenvalues W_i of H . That is, one may write

$$W_i^0 \leq W_i \quad i = 1, 2, 3, \dots \quad (56)$$

this is a consequence of the operator H' being positive definite. Intermediate Hamiltonians, H^k , are constructed such that

$$H^0 \leq H^k \leq H^{k+t} \leq H \quad k, t = 1, 2, 3, \dots \quad (57)$$

The operator inequalities in Eq. (57) mean that for operators $A < B$, $\langle \phi | A | \phi \rangle < \langle \phi | B | \phi \rangle$ for arbitrary ϕ in the domains of A and B . Bazley (17) and Bazley and Fox (18) have given some ways that one may use to construct intermediate Hamiltonians. Then as a result of an

ordering theorem they obtain

$$W_i^0 \leq E_i^k \leq E_i^{k+t} \leq W_i \quad k, t = 1, 2, 3, \dots \quad (58)$$

where the E_i^k and E_i^{k+t} are eigenvalues to the intermediate Hamiltonians. Hence, as one constructs intermediate Hamiltonians which approach the true Hamiltonian, one will obtain E_i^k which serve as lower bounds and approach the true W_i . Two things should be noted however: firstly, the intermediate Hamiltonians must be so constructed that their Schrödinger equations can be solved exactly; and, secondly, if one wishes to obtain a lower bound to the m^{th} state, one must obtain the bounds of all states up to the m^{th} state. The latter is a consequence of the ordering theorem.

An alternative to the intermediate Hamiltonian approach has been suggested by Löwdin (19). His approach involves a so-called bracketing theorem by means of which a lower bound can be determined to an eigenvalue if one has an upper bound. He derives the equation

$$\mathcal{E}_1 = \langle \phi | H + H[P/(\mathcal{E} - H)]H | \phi \rangle \quad (59)$$

where ϕ is a trial function, H is the Hamiltonian and the quantity $P/(\mathcal{E} - H)$ is the reduced resolvent of the problem. If one knows an upper bound \mathcal{E} to the eigenvalue and uses equation (59) one then obtains a lower bound \mathcal{E}_1 . Actually Eq. (59) is written in a symbolic

notation; to write it out is rather complicated. H is first written as $H^0 + V$ and considerations of infinite order perturbation theory are needed, along with many operator inequalities. A brief outline of the method is presented in Appendix III in conjunction with a calculation presented in the next chapter. Suffice it to say here that the method avoids the problem of the ordering theorem, and hence, in theory at least, can be used to determine a lower bound to the m^{th} state directly.

It should be noted here that, unlike the method of intermediate Hamiltonians, the determination of a lower bound depends upon the knowledge of an upper bound. The better the upper bound is known the better the lower bound will be. This has been shown by Reid (20). Choi and Smith (21) have recently applied both the method of intermediate Hamiltonians and the Löwdin procedure to the ground state of He, using the same basis sets, and found that the former yields a better lower bound. Applications of Löwdin's method to excited states have not as yet been published.

It is rather difficult to see how either of these methods, especially Löwdin's method, can be applied simply to more complex systems. Methods which depend upon inner projections of operators onto finite subspaces seem to suffer from a lack of knowledge of the proper functions to span the subspaces in all but the simplest examples.

II. Mathematical Development

II.1 Formulation in Terms of Orbitals

In this chapter a general scheme based on Eq. (1.54) will be developed in the context of orbital theory. It is assumed here that the trial function Φ is an anti-symmetrized product of one electron orbitals or a linear combination of such products, such that Φ possesses a definite orbital and spin angular momentum. The latter means that Φ must be an eigenfunction of the \hat{L}^2 , \hat{S}^2 and \hat{S}_z operators. One term in Φ may thus be represented as

$$\mathcal{A}[\phi_1(1)\alpha(1)\phi_1(2)\beta(2)\phi_2(3)\alpha(3)\phi_2(4)\beta(4)\phi_3(5)\alpha(5)\dots] \quad (1)$$

where \mathcal{A} represents the normalized antisymmetrizer, the ϕ_i are the space functions and the $\alpha(i)$ and $\beta(i)$ are the spin functions. The numbers in parentheses represent the coordinates of the electrons in space and spin space.

If \mathcal{H} is the non-relativistic, spin and time independent Hamiltonian, then the expectation value of \mathcal{H} with respect to Φ is written as

$$E = \langle \mathcal{H} \rangle = \langle \Phi | \mathcal{H} | \Phi \rangle = \langle \Phi | \sum_{\pi} H_{\pi} + \frac{1}{2} \sum_{\sigma \neq \pi} 1/r_{\sigma\pi} | \Phi \rangle \quad (2)$$

where it is assumed that the function Φ is normalized so that $\langle \Phi | \Phi \rangle = 1$. The summations in Eq. (2) are over

all electrons.

The expectation value of \mathcal{H} may be written in the general case, in terms of orbitals as,

$$E = 2 \sum_{\vec{i}} f_i^\lambda H_{\vec{i}\vec{i}} + \sum_{\vec{i}\vec{m}} f_i^\lambda f_m^\mu N_{\vec{i}\vec{i}\vec{m}\vec{m}} \quad (3)$$

where, as in the work of Birss and Fraga (16), f_i^λ is the fractional occupancy of the i^{th} shell of symmetry designation λ . For example, the $2p^2$ configuration will have $f_i^\lambda = f_2^p = 1/3$. The $\sum_{\vec{i}}$ means $\sum_{i\lambda\alpha}$, that is, summation over all orbitals of symmetry species λ and subspecies α and summation over all such symmetry species and subspecies. The forms of $H_{\vec{i}\vec{i}}$ and $N_{\vec{i}\vec{i}\vec{m}\vec{m}}$, along with a more thorough discussion of Eq. (3), are given in Appendix I.

It will be recalled that

$$\Delta = \langle \Phi | (\mathcal{H} - \langle \mathcal{H} \rangle)^2 | \Phi \rangle = \langle \Phi | \mathcal{H}^2 - E^2 | \Phi \rangle ; \quad (4)$$

thus one must also obtain an expression for $\langle \Phi | \mathcal{H}^2 | \Phi \rangle$ in terms of orbitals.

The operator \mathcal{H}^2 is given by

$$\mathcal{H}^2 = \sum_{\pi\sigma} H_\pi H_\sigma + 2 \sum_{\pi} \sum_{\rho<\tau} \frac{H_\pi}{r_{\rho\tau}} + \sum_{\pi<\sigma} \sum_{\rho<\tau} \frac{1}{r_{\pi\sigma}} \frac{1}{r_{\rho\tau}} \quad (5)$$

Now evaluating $\langle \Phi | \mathcal{H}^2 | \Phi \rangle$, where \mathcal{H}^2 is given by Eq. (5) and subtracting from it the square of Eq. (3) one arrives at

$$\Delta = 2 \sum_{\vec{i}} f_i^\lambda X_{\vec{i}} + \sum_{\vec{i}\vec{m}} f_i^\lambda f_m^\mu A_{\vec{i}\vec{m}} + \sum_{\vec{i}\vec{m}\vec{n}} f_i^\lambda f_m^\mu f_n^\nu B_{\vec{i}\vec{m}\vec{n}} + \sum_{\vec{i}\vec{m}\vec{n}\vec{p}} f_i^\lambda f_m^\mu f_n^\nu f_p^\zeta C_{\vec{i}\vec{m}\vec{n}\vec{p}} \quad (6)$$

where the $A_{\vec{i}\vec{m}}$, $B_{\vec{i}\vec{m}\vec{n}}$ and $C_{\vec{i}\vec{m}\vec{n}\vec{p}}$ are linear combinations of integrals which are given in Appendix II along with a derivation of Eq. (6).

It will be recalled that the ϕ which satisfies

$$\delta Z = \delta E + \omega \delta \Delta = 0 \quad (7)$$

will determine the best bounds if $Z = B$ and

$$\omega = \left[\frac{(E - \tilde{E}_\gamma)}{(E - \tilde{E}_\gamma)^2 - \Delta} \right] \text{ or will be the best } \phi_k, \text{ if } Z = Q^2 \text{ and } \omega = \left[\frac{|E - W_k|}{2\Delta} \right].$$

In the orbital approximation this means that the orbitals which determine ϕ must be obtained and that they must be such that the ϕ satisfies Eq. (7). The determination of such orbitals will now be investigated.

The variation in the energy in terms of orbitals can be obtained from Eq. (3) and is given by

$$\delta E = 2 \sum_{\vec{i}} \{ \langle \delta \phi_{\vec{i}} | f_i^\lambda [2\hat{H} + \sum_{\vec{m}} f_m^\mu \hat{N}_{\vec{m}}] | \phi_{\vec{i}} \rangle + \text{c.c.} \} \quad (8)$$

The c.c. represents the complex conjugate of the first term. Likewise the variation in Δ which can be obtained from Eq. (6) is given by

$$\delta \Delta = \sum_{\vec{i}} \{ \langle \delta \phi_{\vec{i}} | f_{\vec{i}}^{\lambda} [2\hat{X} + \sum_{\vec{m}} f_{\vec{m}}^{\mu} \hat{A}_{\vec{m}} + \sum_{\vec{mn}} f_{\vec{m}}^{\mu} f_{\vec{n}}^{\nu} \hat{B}_{\vec{mn}} + \sum_{\vec{mnp}} f_{\vec{m}}^{\mu} f_{\vec{n}}^{\nu} f_{\vec{p}}^{\zeta} \hat{C}_{\vec{mnp}}] | \phi_{\vec{i}} \rangle + \text{c.c.} \} \quad (9)$$

Combining Eqs. (8) and (9) according to Eq. (7) the following is obtained,

$$\delta Z = \sum_{\vec{i}} \{ \langle \delta \phi_{\vec{i}} | f_{\vec{i}}^{\lambda} [2(\hat{H} - \omega \hat{X}) + \sum_{\vec{m}} f_{\vec{m}}^{\mu} (\hat{N}_{\vec{m}} + \omega \hat{A}_{\vec{m}}) + \sum_{\vec{mn}} f_{\vec{m}}^{\mu} f_{\vec{n}}^{\nu} \omega (\hat{B}_{\vec{mn}} + \sum_{\vec{p}} f_{\vec{p}}^{\zeta} \hat{C}_{\vec{mnp}})] | \phi_{\vec{i}} \rangle + \text{c.c.} \} = 0 \quad (10)$$

where the carets over various symbols denote operators. In obtaining equations (3) and (6) it has been assumed that the orbitals are orthonormal; thus one must constrain the variation of the orbitals in Eq. (10) so as to maintain the orthonormality between them. This is accomplished by the technique of using Lagrangian multipliers. Originally the orbitals are such that

$$\langle \phi_{\vec{i}}^{\lambda\alpha} | \phi_{\vec{u}}^{\lambda\alpha} \rangle = \delta_{\vec{i}\vec{u}} \quad (11)$$

but during a variation they must satisfy

$$\langle \delta \phi_{\vec{i}}^{\lambda\alpha} | \phi_{\vec{u}}^{\lambda\alpha} \rangle + \langle \phi_{\vec{i}}^{\lambda\alpha} | \delta \phi_{\vec{u}}^{\lambda\alpha} \rangle = 0 \quad (12)$$

in order to remain orthonormal. Notice that only orbitals of the same symmetry need be considered, because two orbitals of different symmetries are automatically

orthogonal. If the Lagrangian multiplier for the constraint involving orbitals i and u is designated as $\theta_{ui}^{\lambda\alpha}$ and this is multiplied by Eq. (12) and one takes all such products and sums then, one obtains

$$\sum_{\vec{i}u} [\theta_{ui}^{\lambda\alpha} \langle \delta \phi_{\vec{i}} | \phi_u^{\lambda\alpha} \rangle + \theta_{\vec{i}u}^{\lambda\alpha} \langle \delta \phi_{\vec{i}}^* | \phi_u^{*\lambda\alpha} \rangle] = 0 \quad (13)$$

If one designates the operator in Eq. (10) as $F_{\vec{i}}$, then that equation may be rewritten as

$$\delta Z = \sum_{\vec{i}} \{ \langle \delta \phi_{\vec{i}} | F_{\vec{i}} | \phi_{\vec{i}} \rangle + \langle \delta \phi_{\vec{i}}^* | F_{\vec{i}}^\dagger | \phi_{\vec{i}}^* \rangle \} = 0 \quad (14)$$

Now adding Eq. (13) to Eq. (14), one obtains

$$\sum_i \{ \langle \delta \phi_{\vec{i}} | F_{\vec{i}} | \phi_{\vec{i}} \rangle - \sum_u \phi_u^{\lambda\alpha} \theta_{ui}^{\lambda\alpha} \rangle + \langle \delta \phi_{\vec{i}}^* | F_{\vec{i}}^\dagger | \phi_{\vec{i}}^* \rangle - \sum_u \phi_u^{*\lambda\alpha} \theta_{\vec{i}u}^{\lambda\alpha} \rangle \} = 0 \quad (15)$$

Equation (15) will hold for any infinitesimal variation $\delta \phi_{\vec{i}}$, $\delta \phi_{\vec{i}}^*$, and, since the variations among various orbitals are arbitrary and independent, every term in curly brackets in the sum of Eq. (15) must be zero; furthermore, since $\delta \phi_{\vec{i}}$ and $\delta \phi_{\vec{i}}^*$ are independent of one another for a given orbital, each of the two integrals in curly brackets must independently be zero. The only way the integrals can be zero is if either the bra or the ket is zero; the bra cannot be zero since arbitrary variations have been assumed; hence the ket must be zero and one may write

$$F_{\vec{1}} \phi_{\vec{1}} = \sum_{\vec{u}} \phi_{\vec{u}}^{\lambda\alpha} \theta_{\vec{u}\vec{1}}^{\lambda\alpha} \quad (16)$$

$$F_{\vec{1}}^{\dagger} \phi_{\vec{1}}^* = \sum_{\vec{u}} \phi_{\vec{u}}^{*\lambda\alpha} \theta_{\vec{1}\vec{u}}^{\lambda\alpha} . \quad (17)$$

Since the Lagrangian multipliers may be considered as the elements of a Hermitian matrix, Eqs. (16) and (17) are equivalent. If the system under consideration is a closed shell system then the operator designated as $F_{\vec{1}}$ is identical for all orbitals and, hence, need not be subscripted. Thus one may write

$$F \phi_{\vec{1}} = \sum_{\vec{u}} \phi_{\vec{u}}^{\lambda\alpha} \theta_{\vec{u}\vec{1}}^{\lambda\alpha} . \quad (18)$$

If the orbitals are subjected to a unitary transformation so as to diagonalize the matrix of Lagrangian multipliers the following equation is obtained, since the operator F will remain invariant under such a transformation

$$F \phi_{\vec{1}} = \phi_{\vec{1}} \theta_{\vec{1}\vec{1}} , \quad (19)$$

This equation is well known (22) for the case that

$$F = 2\hat{H} + \sum_{\vec{m}} \hat{N}_{\vec{m}} . \quad (20)$$

Here, however

$$\begin{aligned} F = & 2(\hat{H} - \omega\hat{X}) + \sum_{\vec{m}} (\hat{N}_{\vec{m}} + \omega A_{\vec{m}}) \\ & + \sum_{\vec{m}\vec{n}} \omega (\hat{B}_{\vec{m}\vec{n}} + \sum_{\vec{p}} \hat{C}_{\vec{m}\vec{n}\vec{p}}) \end{aligned} \quad (21)$$

for the case of closed shells. Thus with the operator given by Eq. (21), one finds the solutions of Eqs. (19), and the solutions of these equations will be such that the resulting ϕ has the properties previously discussed. If, however, the system under consideration is an open shell system, then one must follow the method of Birss and Fraga (16) and define a general coupling operator $R^{\lambda\alpha}$.

This operator is given by

$$R^{\lambda\alpha} = \sum_{\vec{k}} r_{\vec{k}}^{\lambda\alpha} \quad (22)$$

where

$$\begin{aligned} r_{\vec{k}}^{\lambda\alpha} = r_{\vec{k}} = & |\phi_{\vec{k}}\rangle \langle \phi_{\vec{k}}| F_{\vec{k}}^{\lambda\alpha} - \sum_{\vec{v}} |\phi_{\vec{k}}\rangle \langle \phi_{\vec{k}}| F_{\vec{v}}^{\lambda\alpha} |\phi_{\vec{v}}^{\lambda\alpha}\rangle \langle \phi_{\vec{v}}^{\lambda\alpha}| \\ & + |\phi_{\vec{k}}\rangle \langle \phi_{\vec{k}}| F_{\vec{k}}^{\lambda\alpha} |\phi_{\vec{v}}^{\lambda\alpha}\rangle \langle \phi_{\vec{v}}^{\lambda\alpha}| - \sum_{\vec{v}} |\phi_{\vec{v}}^{\lambda\alpha}\rangle \langle \phi_{\vec{v}}^{\lambda\alpha}| F_{\vec{v}}^{\lambda\alpha} |\phi_{\vec{k}}\rangle \langle \phi_{\vec{k}}| \\ & + (F_{\vec{k}}^{\lambda\alpha} |\phi_{\vec{k}}\rangle \langle \phi_{\vec{k}}| . \end{aligned} \quad (23)$$

In a general open shell case the operator $F_{\vec{k}}^{\lambda\alpha}$ which appears in Eq. (23) is given by

$$\begin{aligned} F_{\vec{k}}^{\lambda\alpha} = & f_{\vec{k}}^{\lambda} \{ 2(\hat{H} - \omega \hat{X}) + \sum_{\vec{m}} f_{\vec{m}}^{\mu} (\hat{N}_{\vec{m}} + \omega \hat{A}_{\vec{m}}) + \sum_{\vec{m}\vec{n}} f_{\vec{m}}^{\mu} f_{\vec{n}}^{\nu} \omega \\ & \times (\hat{B}_{\vec{m}\vec{n}} + \sum_{\vec{p}} f_{\vec{p}}^{\zeta} \hat{C}_{\vec{m}\vec{n}\vec{p}}) \} . \end{aligned} \quad (24)$$

By use of Eq. (23), Eq. (16) may be written in the form

$$R^{\lambda\alpha} \phi_i^{\lambda\alpha} = \phi_i^{\lambda\alpha} \Theta_{ii}^{\lambda\alpha} . \quad (25)$$

Hence the Eqs. (16) have been transformed into pseudo-eigenvalue equations which may be solved by standard iterative techniques. There will be a set of equations like Eqs. (25) for every group of orbitals of symmetry designation $\lambda\alpha, \mu\beta, \dots$. After having determined all these groups of orbitals from the solutions of Eqs. (25), one may then form Φ from these orbitals. This Φ will be the desired solution of Eq. (7) and will hence serve to give the best bound or best Φ_k depending upon the quantities Z and ω .

II.2 Expansion of the ϕ_i in Terms of a Basis Set

The individual orbitals, $\phi_i^{\lambda\alpha}$, may be expanded in terms of a given basis set of functions, $\chi_q^{\lambda\alpha}$, as

$$\phi_i^{\lambda\alpha} = \sum_q \chi_q^{\lambda\alpha} C_{qi}^{\lambda} \quad (26)$$

where the C_{qi}^{λ} are the expansion coefficients. Eq. (26) may also be written more conveniently in matrix notation as

$$\phi_i^{\lambda\alpha} = \vec{\chi}^{\lambda\alpha} \vec{C}_i^{\lambda} \quad (27)$$

where $\vec{\chi}^{\lambda\alpha}$ is a row vector whose elements are the basis functions of symmetry designation $\lambda\alpha$ and \vec{C}_i^{λ} is a column vector whose elements are the coefficients C_{qi}^{λ} . The latter are independent of subspecies designation, as they must be in order to maintain the correct symmetry

transformation properties among the orbitals. Since the orbitals have been assumed orthonormal this leads to

$$\langle \phi_i^{\lambda\alpha} | \phi_j^{\lambda\alpha} \rangle = \int \phi_i^{*\lambda\alpha}(\rho) \phi_j^{\lambda\alpha}(\rho) dV_\rho = \tilde{C}_i^{\lambda\alpha} S^{\lambda\alpha} \tilde{C}_j^{\lambda\alpha} = \delta_{ij} \quad (28)$$

where $S^{\lambda\alpha}$ is the overlap matrix. The elements of the overlap matrix are given by

$$S_{qr}^{\lambda\alpha} = \langle \chi_q^{\lambda\alpha} | \chi_r^{\lambda\alpha} \rangle = \int \chi_q^{*\lambda\alpha}(\rho) \chi_r^{\lambda\alpha}(\rho) dV_\rho. \quad (29)$$

The eigenvalue equations (25) may now be expressed in the form

$$\tilde{R}^{\lambda\alpha} \tilde{C}_i^{\lambda\alpha} = \theta_{ii}^{\lambda\alpha} S^{\lambda\alpha} \tilde{C}_i^{\lambda\alpha} \quad (30)$$

where $\tilde{R}^{\lambda\alpha}$ is the matrix representation of the operator $R^{\lambda\alpha}$, i.e., $R_{qr}^{\lambda\alpha} = \langle \chi_q^{\lambda\alpha} | R^{\lambda\alpha} | \chi_r^{\lambda\alpha} \rangle$, in terms of the basis set of functions. There will be such a set of equations, Eqs. (30), for every symmetry designation $\lambda\alpha$.

In the case of a ϕ which has M occupied orbitals of type $\lambda\alpha$ and N occupied orbitals of type $\mu\beta$, etc. [for the upper bound and best ϕ_k calculations] the first M orbitals of type $\lambda\alpha$ and the first N orbitals of type $\mu\beta$, etc. will be taken from the solutions of Eqs. (30) in order to obtain the proper ϕ . This is because, in these two cases, one is minimizing Z, i.e., minimizing Q^2 in the case of finding the best ϕ_k and minimizing the upper bound, B^u , in the other case. However, in finding the lower bound, B^l , one is maximizing B^l and hence, for a

Φ as described above, one would take the last M orbitals of type $\lambda\alpha$ and the last N orbitals of type $\mu\beta$, etc. in order to obtain the appropriate Φ . This problem of picking the right set of orbitals is of course a consequence of Eq. (26), since if there are M orbitals of type $\lambda\alpha$ the sum over q may run up to $q = U$ where $U > M$.

In terms of the basis functions, the integrals of Appendix II have the following forms

$$I = \int \chi_q^*(\rho) H_\rho \chi_S(\rho) dV_\rho \quad (31)$$

$$II = \int [H_\rho^\dagger \chi_q^*(\rho)] [H_\rho \chi_S(\rho)] dV_\rho \quad (32)$$

$$III = \int \int \chi_q^*(\rho) \chi_S(\rho) (1/r_{\rho\tau}) \chi_u^*(\tau) \chi_W(\tau) dV_\rho dV_\tau \quad (33)$$

$$IV = \int \int \chi_q^*(\rho) \chi_R(\rho) (1/r_{\rho\tau}) \chi_S^*(\tau) [H_\tau \chi_t(\tau)] dV_\rho dV_\tau \quad (34)$$

$$V = \int \int \chi_q^*(\rho) \chi_R(\rho) (1/r_{\rho\tau})^2 \chi_S^*(\tau) \chi_t(\tau) dV_\rho dV_\tau \quad (35)$$

$$VI = \int \int \int \chi_q^*(\rho) \chi_R(\rho) (1/r_{\rho\tau}) \chi_S^*(\tau) \chi_t(\tau) (1/r_{\rho\eta}) \\ \times \chi_u^*(\eta) \chi_V(\eta) dV_\rho dV_\tau dV_\eta. \quad (36)$$

Here the subscripts on the basis functions denote different basis functions of the same symmetry or of different symmetries, i.e., q may be of type $\lambda\alpha$ and r of type $\lambda\alpha$ or $\mu\beta$, etc.

The correspondence between the integrals above and the ones in Appendix II is

$$I \rightarrow H$$

$$II \rightarrow X$$

$$III \rightarrow N$$

$$IV \rightarrow P$$

$$V \rightarrow Q$$

$$VI \rightarrow T \text{ and } Y$$

where it is to be understood that linear combinations of the integrals on the left give the type of integral denoted on the right. The most common type of basis function used in the expansion, Eq. (26), is the Slater-type-orbitals (STO's). A discussion of the various integrals which arise from the forms I - VI for one and two center problems using STO's will now be given.

II.3 Integrals over Slater Basis Functions

One Center Case

For the one center case the one electron operator is given by

$$H_{\rho} = -\frac{\nabla_{\rho}^2}{2} - \frac{Z}{r_{\rho}} \quad (37)$$

where Z is the nuclear charge and r_{ρ} is the distance of the ρ^{th} electron from the nucleus. The two electron operator is $1/r_{\rho\tau}$, where $r_{\rho\tau}$ is the distance between electrons ρ and τ .

Evaluation of the integrals I and III for this case is quite familiar and the techniques are described in standard text books (23). The evaluation of integrals II and IV for the one center case can be accomplished by the same methods used to evaluate I and III with certain obvious modifications; the result of IV is a linear combination of integrals of type III. However, the values of the integrals V and VI for the one center case are not so easily obtained and the method of evaluation not so obvious. An analytic evaluation of V was accomplished by Solony, Lin and Birss (24), and the analytic evaluation of VI will be given here.

As in the work of Solony, Lin and Birss, unnormalized Slater functions are used here:

$$(n, \ell, m) = r^{n-1} e^{-\zeta r} P_{\ell}^{|m|}(\cos \theta) f(|m|\phi) \quad (38)$$

$f = \cos$, for $m \geq 0$; $f = \sin$, for $m < 0$. The integral in question may be rewritten as

$$\begin{aligned} & \langle x_1 x_1' | 1/r_{1c} | x_c x_c' | 1/r_{2c} | x_2 x_2' \rangle = \\ & \langle (n_1, \ell_1, m_1) (n_1', \ell_1', m_1') | 1/r_{1c} | (n_c, \ell_c, m_c) \\ & (n_c', \ell_c', m_c') | 1/r_{2c} | (n_2, \ell_2, m_2) (n_2', \ell_2', m_2') \rangle \\ & = \int \int \int x_1(1) x_1'(1) (1/r_{1c}) x_c(c) x_c'(c) (1/r_{2c}) \\ & x_2(2) x_2'(2) dV_1 dV_c dV_2 \end{aligned} \quad (39)$$

where the subscript and electron label c emphasize the role of these functions, i.e., electrons 1 and 2 interact with electron c but not with each other.

The products $x_1(1)x_1'(1)$, $x_2(2)x_2'(2)$, $x_c(c)x_c'(c)$, can be separately expanded as linear combinations of unnormalized charge distributions $[N_1, L_1, M_1]$, $[N_2, L_2, M_2]$, $[N_c, L_c, M_c]$ with the result that the integral VI becomes a linear combination of integrals over basic charge distributions, of the form

$$\begin{aligned}
 & \langle N_1, L_1, M_1 | 1/r_{1c} | N_c, L_c, M_c | 1/r_{2c} | N_2, L_2, M_2 \rangle \\
 &= \int \frac{r_1^{N_1-1}}{r_{1c}} e^{-2\bar{\zeta}_1 r_1} P_{L_1}^{|M_1|}(\cos \theta_1) f(|M_1| \phi_1) dV_1 \\
 & \quad \times \int \frac{r_c^{N_c-1}}{r_{1c}} e^{-2\zeta_c r_c} P_{L_c}^{|M_c|}(\cos \theta_c) f(|M_c| \phi_c) dV_c \\
 & \quad \times \int \frac{r_2^{N_2-1}}{r_{2c}} e^{-2\bar{\zeta}_2 r_2} P_{L_2}^{|M_2|}(\cos \theta_2) f(|M_2| \phi_2) dV_2 \quad (40)
 \end{aligned}$$

with $\bar{\zeta}_i = (\zeta_i + \zeta_i')/2$.

Two reasonably distinct methods of evaluating these integrals have been investigated. In one of these, the integrals over electrons 1 and 2 in Equation (40) are evaluated by the scheme given by Roothaan (25), yielding functions of electron c . Combination of these functions with the charge distribution for electron c , and evaluating the remainder of Equation (40) leads to, among others,

the integral

$$\int_0^\infty r_c^{N_c - L_1 - L_2 - 1} e^{-2(\bar{\zeta}_c + \bar{\zeta}_1 + \bar{\zeta}_2)r_c} dr_c$$

Unfortunately there are cases of interest for which $N_c - L_1 - L_2 - 1$ is negative. In the second method, $1/r_{ic}$ is expanded in spherical harmonics and the radial variables $r_<$ and $r_>$, the lesser and greater of r_i and r_c . This requires that the integration limits for r_1 and r_2 depend upon r_c . Comparison of the two methods led to the conclusion that the difficulty essentially arises because one introduces an infinity when evaluating, e.g.,

$$\int_0^{r_c} f(r_1) dr_1 = \int_0^\infty f(r_1) dr_1 - \int_{r_c}^\infty f(r_1) dr_1 \quad (41)$$

a technique which leads to forms identical to those of Roothaan at the stage just before integration over electron c. Therefore a modification of the second technique was adopted; it avoids the introduction of the infinity by a reversal of the order of integration.

Integration

The operator $1/r_{ic}$ is expanded as

$$\begin{aligned} 1/r_{ic} = & \sum_{k=0}^{\infty} \sum_{m=0}^k \frac{(k-m)!}{(k+m)!} (2-\delta_{m0}) \left[\frac{r_<^k}{r_>^{k+1}} \right]_{i,c} P_k^m(\cos \theta_i) \\ & \times P_k^m(\cos \theta_c) \cos m(\phi_i - \phi_c) \end{aligned} \quad (42)$$

where $r_<$ and $r_>$ are the lesser and greater, respectively, of r_i and r_c . Substitution of this form for $1/r_{1c}$ into Equation (40) introduces the factor

$$\begin{aligned} & \int_0^\pi P_{L_1}^{|M_1|}(\cos \theta_1) P_k^m(\cos \theta_1) \sin \theta_1 d\theta_1 \int_0^{2\pi} f(|M_1| \phi_1) \\ & \quad \times \cos m(\phi_1 - \phi_c) d\phi_1 \\ &= \frac{2\pi(1 + \delta_{M_1 0})}{2L_1 + 1} \frac{(L_1 + |M_1|)!}{(L_1 - |M_1|)!} \delta_{kL_1} \delta_{m|M_1|} f(|M_1| \phi_c). \end{aligned}$$

Only the term with $k = L_1$, $m = |M_1|$ subsists in $1/r_{1c}$, and that with $k = L_2$, $M = |M_2|$ in $1/r_{2c}$, so that Equation (40) becomes

$$\begin{aligned} U = & \frac{16\pi^2 [\theta] [\phi]}{(2L_1+1)(2L_2+1)} \int r_1^{N_1+1} e^{-2\bar{\zeta}_2 r_1} \left[\frac{r_<^{L_1}}{r_>^{L_1+1}} \right]_{1,c} dr_1 \\ & \times \int r_c^{N_c+1} e^{-2\bar{\zeta}_c r_c} dr_c \int r_2^{N_2+1} e^{-2\bar{\zeta}_2 r_2} \left[\frac{r_<^{L_2}}{r_>^{L_2+1}} \right]_{2,c} dr_2 \end{aligned} \quad (43)$$

with

$$\begin{aligned} [\theta] = & \int_0^\pi P_{L_1}^{|M_1|}(\cos \theta_c) P_{L_2}^{|M_2|}(\cos \theta_2) P_{L_c}^{|M_c|}(\cos \theta_c) \\ & \times \sin \theta_c d\theta_c \end{aligned} \quad (44)$$

$$[\phi] = \int_0^{2\pi} f(|M_1| \phi_c) f(|M_2| \phi_c) f(|M_c| \phi_c) d\phi_c. \quad (45)$$

Four distinct cases can be distinguished, arising from various assignments of $r_>$, and $r_<$:

$$A: r_{<1,c} = r_c, r_{>1,c} = r_1; r_{<2,c} = r_c, r_{>2,c} = r_2$$

$$B: r_{<1,c} = r_c, r_{>1,c} = r_1; r_{<2,c} = r_2, r_{>2,c} = r_c$$

$$C: r_{<1,c} = r_1, r_{>1,c} = r_c; r_{<2,c} = r_c, r_{>2,c} = r_2$$

$$D: r_{<1,c} = r_1, r_{>1,c} = r_c; r_{<2,c} = r_2, r_{>2,c} = r_c.$$

For case A the radial integrals of Equation (43) give

$$\begin{aligned} I_A &= \int_0^\infty r_c^{N_c+L_1+L_2+1} e^{-2\bar{\zeta}_c r_c} dr_c \int_{r_c}^\infty r_1^{N_1-L_1} e^{-2\bar{\zeta}_1 r_1} dr_1 \\ &\quad \times \int_{r_c}^\infty r_2^{N_2-L_2} e^{-2\bar{\zeta}_2 r_2} dr_2 \\ &= \frac{(N_1-L_1)!(N_2-L_2)!}{\omega_1^{N_1-L_1+1} \omega_2^{N_2-L_2+1} \sigma^{N_c+N_1+N_2+4}} \sum_{k=0}^{N_1-L_1} \frac{\omega_1^k}{k!} \sum_{\ell=0}^{N_2-L_2} \omega_2^\ell \\ &\quad \times \frac{(N_c+L_1+L_2+k+\ell+1)!}{\ell!} \end{aligned} \quad (46)$$

with

$$\omega_i = 2\bar{\zeta}_i/\sigma, \quad \sigma = 2(\bar{\zeta}_c + \bar{\zeta}_1 + \bar{\zeta}_2).$$

For case B,

$$\begin{aligned} I_B &= \int_0^\infty r_c^{N_c+L_1-L_2} e^{-2\bar{\zeta}_c r_c} dr_c \int_{r_c}^\infty r_1^{N_1-L_1} e^{-2\bar{\zeta}_1 r_1} dr_1 \int_0^{r_c} \\ &\quad \times r_2^{N_2+L_2+1} e^{-2\bar{\zeta}_2 r_2} dr_2 \end{aligned}$$

$$\begin{aligned}
 &= (N_1 - L_1)! (N_2 + L_2 + 1)! \left\{ \frac{1}{\mu_{11}^{N_1 - L_1 + 1} \mu_{21}^{N_2 + L_2 + 2} \rho_1^{N_c + N_1 - N_2 + 4}} \sum_{k=0}^{N_1 - L_1} \right. \\
 &\quad \times \frac{(N_c + L_1 - L_2 + k)!}{k!} \mu_{11}^k \\
 &\quad - \frac{1}{\omega_1^{N_1 - L_1 + 1} \omega_2^{N_2 + L_2 + 2} \sigma^{N_c + N_1 + N_2 + 4}} \sum_{k=0}^{N_2 - L_2} \frac{\omega_1^k}{k!} \sum_{\ell=0}^{N_2 + L_2 + 1} \\
 &\quad \times \left. \frac{(N_c + L_2 - L_2 + k + \ell)!}{\ell!} \omega_2^\ell \right\} \quad (47)
 \end{aligned}$$

with $\mu_{ij} = 2 \bar{\zeta}_i / \rho_i$, $\rho_i = 2(\bar{\zeta}_c + \bar{\zeta}_i)$.

For case C the form is that of case B with labels 1 and 2 interchanged throughout. In both of these cases use of Equation (41) has been made since the critical exponents of r_c , $N_c + L_1 - L_2$ or $N_c - L_1 + L_2$, cannot become negative (this is a result of the inequality given in Equation (52)).

In case D,

$$\begin{aligned}
 I_D = & \int_0^\infty r_c^{N_c - L_1 - L_2 - 1} e^{-2\bar{\zeta}_c r_c} dr_c \int_0^{r_c} r_1^{N_1 + L_1 + 1} e^{-2\bar{\zeta}_1 r_1} dr_1 \\
 & \times \int_0^{r_c} r_2^{N_2 + L_2 + 1} e^{-2\bar{\zeta}_2 r_2} dr_2;
 \end{aligned}$$

this is the only term giving rise to the difficulty discussed in the introduction. To obviate the trouble

one can change the integration variables and then the order of integration to obtain

$$\begin{aligned}
 I_D &= \int_0^\infty r_c^{N_c+N_1+N_2+3} e^{-2\bar{\zeta}_c r_c} dr_c \int_0^1 x^{N_1+L_1+1} e^{-2\bar{\zeta}_1 r_c x} dx \int_0^1 \\
 &\quad \times y^{N_2+L_2+1} e^{-2\bar{\zeta}_2 r_c y} dy \\
 &= \int_0^1 x^{N_1+L_1+1} dx \int_0^1 y^{N_2+L_2+1} dy \int_0^\infty r_c^{N_c+N_1+N_2+3} \\
 &\quad \times e^{-2(\bar{\zeta}_c+\bar{\zeta}_1 x+\bar{\zeta}_2 y)r_c} dr_c \\
 &= \frac{(N_c+N_1+N_2+3)!}{2^{N_c+N_1+N_2+4} \bar{\zeta}_1^{N_1+L_1+2} \bar{\zeta}_2^{N_2+L_2+2}} \sum_{k=0}^{N_1+L_1+1} \binom{N_1+L_1+1}{k} \frac{(-1)^k}{N_c-L_1+N_2+2+k} \\
 &\quad \times \sum_{\ell=0}^{N_2+L_2+1} \binom{N_2+L_2+1}{\ell} (-1)^\ell \left\{ \bar{\zeta}_c^\ell \left[\frac{1}{\bar{\zeta}_c} N_c-L_1-L_2+\ell \right. \right. \\
 &\quad \left. \left. - 1/(\bar{\zeta}_c+\bar{\zeta}_2) N_c-L_1-L_2+\ell \right] / (N_c-L_1-L_2+\ell)^* \right. \\
 &\quad \left. - (\bar{\zeta}_c+\bar{\zeta}_1)^\ell \sum_{m=0}^k \binom{k}{m} (-\bar{\zeta}_1)^m \left[\frac{1}{(\bar{\zeta}_c+\bar{\zeta}_1)} N_c-L_1-L_2+\ell+m \right. \right. \\
 &\quad \left. \left. - 1/(\bar{\zeta}_c+\bar{\zeta}_1+\bar{\zeta}_2) N_c-L_1-L_2+\ell+m \right] / (N_c-L_1-L_2+\ell+m)^{**} \right\} \quad (48)
 \end{aligned}$$

The asterisk indicates that when $N_c-L_1-L_2+\ell = 0$, it and the preceding term in square brackets are replaced by $\ln[(\bar{\zeta}_c+\bar{\zeta}_1)/\bar{\zeta}_c]$; similarly for the double asterisk, if $N_c-L_1-L_2+\ell+m = 0$, it and the preceding term in square

brackets are replaced by $\ln[(\bar{\zeta}_c + \bar{\zeta}_1 + \bar{\zeta}_2)/(\bar{\zeta}_c + \bar{\zeta}_1)]$.

If N_c , L_1 and L_2 are such that $N_c - L_1 - L_2 - 1$ is positive, the method of Equation (41) can be used to evaluate I_D ,

$$I_D = \frac{(N_1 + L_1 + 1)! (N_2 + L_2 + 1)!}{2^{N_c + N_1 + N_2 + 4} \bar{\zeta}_1^{N_1 + L_1 + 2} \bar{\zeta}_2^{N_2 + L_2 + 2}} \left\{ \frac{(N_c - L_1 - L_2 - 1)!}{\bar{\zeta}_c^{N_c - L_1 - L_2}} \right. \\ \times \sum_{k=0}^{N_1 + L_1 + 1} \frac{(N_c - L_1 - L_2 + k - 1)!}{k! (\bar{\zeta}_c + \bar{\zeta}_1)^{N_c - L_1 - L_2}} \mu_{11}^k - \sum_{k=0}^{N_2 + L_2 + 1} \frac{(N_c - L_1 - L_2 + k - 1)!}{k! (\bar{\zeta}_c + \bar{\zeta}_2)^{N_c - L_1 - L_2}} \mu_{22}^k \\ \left. + \sum_{k=0}^{N_1 + L_1 + 1} \frac{\omega_1^k}{k!} \sum_{\ell=0}^{N_2 + L_2 + 1} \frac{(N_c - L_1 - L_2 + k + \ell - 1)!}{\ell!} \omega_2^\ell \right\} \quad (49)$$

The formulae given above were checked in a number of ways. Using the alternate form for I_D , Equation (49), the analytic form of U derived here was checked against a number of specific formulae obtained by the use of the Roothaan scheme. Two versions of a computer program were made, using Equations (48) and (49) for I_D . Where (49) was applicable, the two methods agreed. Numerical differentiation was used in conjunction with the program using Equation (48) to raise the quantum numbers of the various charge distributions. Agreement between values obtained in this way and by calculation using the raised quantum numbers in Equations (46) to (48) was found. In particular, in those cases where N_c was raised from a condition where the logarithmic terms

entered to a high enough value that they no longer occurred, the agreement can be taken as guaranteeing the validity of Equation (48).

The Angular Integrations

The integrals $[\theta]$ and $[\phi]$ of Equations (44) and (45) are well known in the theory of vector coupling. $[\phi]$ is zero if one of M_1, M_2, M_c is negative, or if all three are negative or if the equality

$$|M_i| + |M_j| = |M_k|$$

is not satisfied by some assignment of 1, 2, and c to i, j, and k. Then

$$[\phi] = 2\pi, M_i = M_j = M_k = 0$$

$$= \pi, M_i = M_j \neq 0, M_k = 0$$

$$= -\pi/2, M_i \neq M_j, M_i < 0, M_j < 0, M_k > 0,$$

$$M_i + M_j = M_k$$

$$= \pi/2, \text{ for all } M_i \neq 0, \text{ the } M_i \text{ not satisfying the above conditions,}$$

One possible form of $[\phi]$ is (26)

$$\int P_{\ell}^i(\cos \phi) P_m^j(\cos \phi) P_n^k(\cos \phi) \sin \phi d\phi$$

$$= (-1)^{(\ell-m+n)/2-k}$$

$$\times \frac{(m+j)!(n+k)!(\ell+m-n)!((\ell+m+n)/2)!}{(m-j)!(\ell+m+n+1)!((\ell+m-n)/2)!((\ell-m+n)/2)!((- \ell+m+n)/2)!}$$

$$\times \sum_p (-1)^p \frac{(\ell+i+p)!(m+n-i-p)!}{p!(\ell-i-p)!(n-k-p)!(m-n+i+p)!} \quad (51)$$

with the restrictions

$$i + j = k, m + n > \ell > m - n, m > n. \quad (52)$$

This completes the discussion of the evaluation of integral VI and with its evaluation all the integrals necessary to carry out a calculation involving Δ on any atom are now available. Hence the methods described in Chapter I and developed in this chapter in terms of orbital theory can be applied to any atom, so long as the orbitals are given by linear combinations of STO's. However, this situation does not exist for diatomic molecules, as will be shown below.

Two Center Case

For the two center problem, the one electron operator is given by

$$H_\rho = -\frac{\nabla_\rho^2}{2} - \frac{Z_A}{r_{\rho A}} - \frac{Z_B}{r_{\rho B}} = -\frac{\nabla_\rho^2}{2} - \frac{Z_A}{r_A} - \frac{Z_B}{r_B} \quad (53)$$

where Z_A and Z_B are the nuclear charges of nuclei A and B respectively, and where $r_{\rho A} = r_A$ and $r_{\rho B} = r_B$ are

the distances between electron ρ and nuclei A and B respectively.

Evaluation of integrals I and II for the two center case has been accomplished (25, 27). In the integral forms I, II and IV, H appears where χ is a STO with orbital exponent α and H is as given in Eq. (53).

$$H\chi = \left[\frac{-n(n-1) - l(l+1)}{2r^2} + \frac{\alpha - Z}{r} - \frac{\alpha^2}{2} \right] \chi \quad (54)$$

which shows that the one electron operator acting upon an STO produces a linear combination of STO's. Thus the integrals having the form I can be expressed in terms of the familiar overlap type. The integrals having the form III are of three types:

- (1) $\langle \chi_A \chi'_A | 1/r_{12} | \chi''_B \chi'''_B \rangle$, coulomb type
- (2) $\langle \chi_A \chi'_B | 1/r_{12} | \chi''_B \chi'''_A \rangle$, exchange type, and
- (3) $\langle \chi_A \chi'_A | 1/r_{12} | \chi''_A \chi'''_B \rangle$, hybrid type.

(55)

Where the A and B denote the nuclei on which the STO is centered.

In considering integrals of the form II, the following types occur, as can be seen by using Eqs. (53) and (54),

$$(1) \quad \langle \chi_A | 1/r_A^m r_B^n | \chi_B \rangle$$

$$(2) \quad \langle \chi_A | 1/r_A^m r_B^n | \chi_A \rangle \quad (56)$$

where $m, n = 0, 1, 2$ and $m + n \leq 2$. These integrals have been evaluated analytically (24, 28).

For the integrals of the form IV, three types exist

$$(1) \quad \langle \chi_A \chi_A' | 1/r_{12} | \chi_B'' \chi_B''' \rangle, \quad \text{a coulomb type}$$

$$(2) \quad \langle \chi_A \chi_B' | 1/r_{12} | \chi_B'' \chi_A''' \rangle, \quad \text{an exchange type, and} \quad (57)$$

$$(3) \quad \langle \chi_A \chi_A' | 1/r_{12} | \chi_A'' \chi_B''' \rangle, \quad \text{a hybrid type.}$$

Each of these integrals, as a result of Eq. (54), will be a linear combination of integrals of the corresponding type given in (55). Hence the evaluation of the basic integrals involved in forms I-IV has been accomplished. However the forms V and VI are considerably more difficult and no analytic expressions have been derived to evaluate these integrals as yet. The various types of integrals which must be evaluated as a result of the forms of V and VI will be briefly considered.

For the integrals of form V, again three types of integrals will arise:

$$(1) \quad \langle \chi_A \chi_A' | (1/r_{12})^2 | \chi_B'' \chi_B''' \rangle$$

$$(2) \quad \langle x_A x_B' | (1/r_{12})^2 | x_B'' x_B''' \rangle \quad (58)$$

$$(3) \quad \langle x_A x_A' | (1/r_{12})^2 | x_A'' x_B''' \rangle .$$

The difficulty in evaluating these integrals arises from the $(1/r_{12})^2$ expansion onto two centers.

For the integrals of the form VI, the following types arise,

$$(1) \quad \langle x_A x_A^I | 1/r_{12} | x_A^{II} x_A^{III} | 1/r_{13} | x_A^{IV} x_B^V \rangle$$

$$(2) \quad \langle x_A x_A^I | 1/r_{12} | x_A^{II} x_B^{III} | 1/r_{13} | x_A^{IV} x_A^V \rangle$$

$$(3) \quad \langle x_A x_A^I | 1/r_{12} | x_A^{II} x_A^{III} | 1/r_{13} | x_B^{IV} x_B^V \rangle$$

$$(4) \quad \langle x_A x_B^I | 1/r_{12} | x_A^{II} x_A^{III} | 1/r_{13} | x_B^{IV} x_A^V \rangle \quad (59)$$

$$(5) \quad \langle x_A x_A^I | 1/r_{12} | x_B^{II} x_B^{III} | 1/r_{13} | x_A^{IV} x_B^V \rangle$$

$$(6) \quad \langle x_A x_B^I | 1/r_{12} | x_B^{II} x_B^{III} | 1/r_{13} | x_A^{IV} x_A^V \rangle$$

$$(7) \quad \langle x_A x_A^I | 1/r_{12} | x_A^{II} x_B^{III} | 1/r_{13} | x_B^{IV} x_A^V \rangle$$

$$(8) \quad \langle x_A x_B^I | 1/r_{12} | x_A^{II} x_B^{III} | 1/r_{13} | x_A^{IV} x_B^V \rangle .$$

Thus in order to apply the methods discussed to a diatomic species with three or more electrons the eleven integrals of (58) and (59) must still be evaluated. This is obviously a place where further work is desirable.

Considering the difficulty involved in evaluating three and four center integrals of \mathcal{H} over STO's the number and difficulty of integrals involving \mathcal{H}^2 would seem to preclude any thought of extending methods involving \mathcal{H}^2 to polyatomic systems, until a thorough investigation of these methods on one and two center problems has been carried out.

Thus the methods described in the preceeding sections are at present limited to atoms and one electron diatomic species.

III. Calculations on the H_2^+ and He Systems

III.1 Introduction

In section 2 the ground state of the H_2^+ system is considered and results are obtained and compared for the lower bounds obtained by three variational schemes: E minimization, the Δ minimization scheme of Fraga and Birss (16) and the lower bound maximization scheme described in the last chapter.

In section 3 upper and lower bounds are obtained for some $3,1P(1s,np)$ excited states of He. The upper bound results are compared with upper bounds obtained by Davidson (30) for these excited states.

The method proposed for obtaining the best ϕ_k for an excited state is applied to the $3,1P(1s,np)$ excited states of He in section 4. These wave functions are tabulated there.

The wave functions obtained in sections 3 and 4 are used in section 5 to calculate some physical properties of the He excited states. These properties are tabulated and a discussion of the results is included.

In section 6 a Hylleraas type calculation is carried out for the ground state of He in order to provide a direct comparison between the method proposed by Löwdin for lower bounds and the method proposed in this work.

III.2 Calculations on the H_2^+ Ground State

In this section the results of the application of the method developed in Chapter I to the H_2^+ ground state will be presented. In applying the formalism for lower bounds the most practical method is the expansion of the orbitals in some suitable basis set, $\chi_p^{\lambda\alpha}$, as mentioned in section II.2. One may write

$$\phi_i^{\lambda\alpha} = \sum_p c_{ip}^{\lambda} \chi_p^{\lambda\alpha}. \quad (1)$$

Equation (2.25) can be expressed in terms of the linear coefficients, c_{ip} , and the matrix representations of the $R^{\lambda\alpha}$ operator under the basis set, as given in Eq. (2.30). The procedure is then the familiar one of any iterative self-consistency approach, with the solutions of the pseudo-eigenvalue equations being used to construct the operator (or its matrix representation), until self-consistency is attained. The resultant orbitals are then used to calculate B, the lower bound, as given by Eq. (1.48).

It should be noted that the upper bound for the ground state as given by Eq. (1.48) reduces to the ordinary variational principle when $\tilde{E}_\gamma = -\infty$, which is the proper choice of \tilde{E}_γ for calculations that are to determine the upper bound for the ground state. Thus, since the upper bound in this case is determined by

the variational method for lowest states, only the lower bound need be considered here.

The trial function used is a generalization of the James function (31),

$$\phi = e^{-\alpha\xi} \sum_i c_i \eta^{2i} \quad (2)$$

where ξ and η are the variables in the confocal elliptic coordinate system. The integrals were evaluated using, in part, the analytic forms of Goodisman and Secrest (9). Besides the method developed in this work, functions obtained by the scheme of Fraga and Birss and by the ordinary variational principle were also used to obtain a lower bound to the ground state. All three methods are used to obtain the molecular orbital ϕ for the H_2^+ ground state and these ϕ 's are then used in the Weinstein formula, Eq. (1.5) and the Temple formula, Eq. (1.48) in order to obtain the lower bound. The three methods each yield a different ϕ and therefore give different lower bounds. The results are tabulated in Table 1. The variational schemes designated as E, Δ and B are the ordinary variational principle, the Δ minimization scheme of Fraga and Birss and the lower bound maximization procedure proposed in this thesis, respectively. It is clear from the results that the scheme proposed here, used in conjunction with the Temple formula gives the best lower bound. B_{Temple} and $B_{\text{Weinstein}}$ give the bound as

Table 1

Comparison of Lower Bounds

No. Basis Functions	Δ	$B_{\text{Weinstein}}$	B_{Temple}	α	Variational Scheme
1	0.091676	-1.38116	-1.20615	1.400	Δ
2	0.001422	-1.14009	-1.10430	1.355	E
2	0.001272	-1.13797 (-1.14724)*	-1.10403 (-1.10706)*	1.340	Δ
2	0.001444	-1.13994	-1.10388	1.320	B
3	0.000903	-1.13251	-1.10367	1.355	E
3	0.000519	-1.12511	-1.10303	1.335	Δ
3	0.000790	-1.12991	-1.10286	1.310	B
4	0.000915	-1.13270	-1.10369	1.355	E
4	0.000519	-1.12511	-1.10303	1.335	Δ
4	0.000790	-1.12991	-1.10286	1.310	B
5	0.000915	-1.13270	-1.10369	1.355	E
5	0.000518	-1.12509	-1.10303	1.335	Δ
5	0.000790	-1.12991	-1.10286	1.310	B

true eigenvalue = -1.10263

* Values obtained by Goodisman and Secrest (9) using their Δ minimization scheme.

calculated from the Temple formula and Weinstein formula respectively. For the Temple bound the value of \tilde{E}_1 was taken as -0.36087 a.u., the exact eigenvalue for the first excited state of \sum_g^+ symmetry at 2 a.u. inter-nuclear separation.

The second best value of the lower bound is obtained by a modification of the method of Fraga and Birss, i.e., by minimizing Δ , as they suggest, but using the Temple formula instead of the Weinstein formula to calculate the lower bound. The lower bound obtained from the wave function determined by the ordinary variational principle is consistently the poorest value.

The convergence of the lower bound with increasing number of basis functions is quite rapid. As seen in Table 1 there is essentially no difference between the results when going from three to five basis functions; hence these values may be considered to be the best lower bounds obtainable with the particular form of trial function chosen.

The advantage of a self-consistent iterative scheme such as the one proposed here and the scheme of Fraga and Birss is clearly shown when the results obtained for two basis functions are compared to a calculation carried out by Goodisman and Secrest (9). The latter calculation was based on two terms of Eq. (1) and a two dimensional grid over α and c_1/c_0 , to obtain the minimum

of Δ . Their results are included in Table 1, in parentheses. It is readily seen that their values are much poorer than the true values obtained by finding the proper minimum of Δ by the scheme of Fraga and Birss. The method of Goodisman and Secrest also cannot be extended easily to more than two basis functions. Hence the desirability of using a direct variational approach (such as the one of Fraga and Birss, which automatically determines the best coefficients and is readily extended to any number of basis functions) cannot be overemphasized.

III.3 Upper and Lower Bounds to He Excited States

In these calculations, basis functions of the type used by Davidson (30) were employed. This was done because the functions are relatively simple and also the results obtained here for the upper bounds could be compared to those obtained by Davidson's method.

The basis functions for the excited states were taken as

$$\chi_{s,n} = \frac{(2\eta_s)^{\frac{3}{2}}}{(n+1)!2^{n+1}} (2\eta_s r)^{n-1} \exp(-\eta_s r) Y_{0,0}(\theta, \phi) \quad n = 1, 2, 3, 4 \quad (3)$$

$$\chi_{p,n} = \frac{(2\eta_p)^{\frac{3}{2}}}{(n+1)!2^{n+1}} (2\eta_p r)^n \exp(-\eta_p r) Y_{1,M}(\theta, \phi) \quad n = 2, 3, 4, 5 \quad (4)$$

where the $\chi_{s,n}$ are the basis functions for the s orbital and the $\chi_{p,n}$ those for the p orbital. The s and p

orbitals were each represented by four basis functions and those functions used for the calculations are given in Eqs. (3) and (4) by the n values. That is, the s and p orbitals are given by

$$\phi_s = \sum_{n=1}^4 c_{s,n} \chi_{s,n}$$

$$\phi_p = \sum_{n=2}^5 c_{p,n} \chi_{p,n}$$

Although the $\{\chi_{s,n}\}$ and $\{\chi_{p,n}\}$ are the same, except for the choice of η_s and η_p , for all the excited state calculations reported here, the $c_{s,n}$ and $c_{p,n}$ of course differ for each calculation. They are determined by the direct application of the method developed in Chapter II for the determination of the best bounds. Further the η 's were varied such that their optimum values give the best bounds obtainable from a wave function of the type considered here. The expansion coefficients and the optimum values of the η 's are given in Tables 2 and 3 for the singlet and triplet states respectively. The U or L in parentheses after the state designation in the tables indicate whether the wave function corresponds to that of an upper or lower bound value respectively.

The values of the upper and lower bounds calculated from these wave functions are given in Table 4 along with the experimental energies and the values obtained

Table 2

Singlet Excited State Wave Functions - Bound Method

ϕ_s			ϕ_p		
n	η	c_n	n	η	c_n
$^1P \ 1s2p \ (L)$					
1	2.19	0.87274	2	0.368	-0.02899
2	2.19	0.13117	3	0.368	0.02990
3	2.19	0.01544	4	0.368	0.99266
4	2.19	0.00195	5	0.368	0.00057
$^1P \ 1s3p \ (U)$					
1	2.19	0.87274	2	0.364	-0.04185
2	2.19	0.13117	3	0.364	0.00600
3	2.19	0.01544	4	0.364	1.03134
4	2.19	0.00195	5	0.364	-0.00699
$^1P \ 1s3p \ (L)$					
1	2.13	0.90986	2	0.269	0.01350
2	2.13	0.09619	3	0.269	-0.02806
3	2.13	0.00800	4	0.269	-0.94830
4	2.13	0.00068	5	0.269	1.86615
$^1P \ 1s4p \ (L)$					
1	2.13	0.90986	2	0.180	-0.07002
2	2.13	0.09619	3	0.180	1.10376
3	2.13	0.00800	4	0.180	-3.40898
4	2.13	0.00068	5	0.180	3.30019

Table 3

Triplet Excited State Wave Functions - Bound Method

ϕ_s			ϕ_p		
n	η	c_n	n	η	c_n
$^3P \ 1s2p \ (L)$					
1	1.76	1.21140	2	0.377	-0.07442
2	1.76	-0.28595	3	0.377	0.23490
3	1.76	0.05236	4	0.377	0.84289
4	1.76	-0.00705	5	0.377	-0.00950
$^3P \ 1s3p \ (U)$					
1	1.76	1.21140	2	0.376	-0.10792
2	1.76	-0.28595	3	0.376	0.26166
3	1.76	0.05237	4	0.376	0.78938
4	1.76	-0.00706	5	0.376	0.04704
$^3P \ 1s3p \ (L)$					
1	1.85	1.12406	2	0.276	0.03428
2	1.85	-0.15784	3	0.276	-0.17941
3	1.85	0.01740	4	0.276	-0.60847
4	1.85	-0.00153	5	0.276	0.16616
$^3P \ 1s4p \ (L)$					
1	1.86	1.11500	2	0.186	-0.12947
2	1.86	-0.14535	3	0.186	1.27357
3	1.86	0.01489	4	0.186	-3.73863
4	1.86	-0.00122	5	0.186	3.45304

Table 4

Upper and Lower Bounds to Some He Excited States*

<u>State</u>	<u>Exp. Energy</u>	<u>Lower Bound</u>	<u>Upper Bound</u>	<u>E_{variational}</u>	<u>E'_{variational}</u>
$^1\text{P} (1s2p)$	-2.12387	-2.12630	-2.12246	-2.12246	-2.12246
$^1\text{P} (1s3p)$	-2.05517	-2.05553	-2.05442	-2.05473	-2.05474
$^1\text{P} (1s4p)$	-2.03110	-2.03159		-2.03089	-2.03089
$^3\text{P} (1s2p)$	-2.13320	-2.13618	-2.13134	-2.13134	-2.13143
$^3\text{P} (1s3p)$	-2.05811	-2.05851	-2.05727	-2.05750	-2.05759
$^3\text{P} (1s4p)$	-2.03235	-2.03272		-2.03199	-2.03208

* In all cases the bounds were calculated using experimental energies for \tilde{E}_γ , (32); the values for the $^1\text{P}(1s5p)$ and $^3\text{P}(1s5p)$ states are -2.02009 and -2.02073 respectively.

by using Davidson's method with the basis set discussed above ($E_{\text{variational}}$), and with a larger basis set ($E'_{\text{variational}}$). A discussion of Davidson's method is in order now before continuing.

Outline of Davidson's Method

For the two electron problem considered here the trial function may be written as

$$\phi^{1,3} = 1/\sqrt{2} [\phi_s(1)\phi_p(2) \pm \phi_p(1)\phi_s(2)] \quad (7)$$

where ϕ_s and ϕ_p are as given in Eqs. (5) and (6);

$\phi_s = \vec{c}_s^\dagger \vec{\chi}_s$ and $\phi_p = \vec{c}_p^\dagger \vec{\chi}_p$. Following the usual notation

$$H = H_1(1) + H_1(2) + 1/r_{12} \quad (8)$$

$$H_{ij} = \int \vec{\chi}_i^\dagger H_1 \vec{\chi}_j d\tau \quad (9)$$

$$S_{ij} = \int \vec{\chi}_i^\dagger \vec{\chi}_j d\tau \quad (10)$$

$$J_s = \int \vec{\chi}_p(1) \vec{\chi}_s^\dagger(2) \vec{c}_s r_{12}^{-1} \vec{c}_s^\dagger \vec{\chi}_s(2) \vec{\chi}_p^\dagger(1) d\tau_1 d\tau_2 \quad (11)$$

$$K_s = \int \vec{\chi}_p(1) \vec{\chi}_s(1) \vec{c}_s r_{12}^{-1} \vec{c}_s^\dagger \vec{\chi}_s(2) \vec{\chi}_p^\dagger(2) d\tau_1 d\tau_2 \quad (12)$$

with similar definitions for J_p and K_p . Minimizing the average energy, $\langle \phi | H | \phi \rangle$, with respect to the coefficients yields Roothaan's (33) pseudoeigenvalue equations

$$(H'_s + \epsilon_p S_{ss}) \vec{c}_s = E (S_{ss} + S_{sp} \vec{c}_p \vec{c}_p^\dagger S_{ps}) \vec{c}_s \quad (13)$$

$$(H'_p + \epsilon_s S_{pp}) \vec{c}_p = E (S_{pp} + S_{ps} \vec{c}_s \vec{c}_s^\dagger S_{sp}) \vec{c}_p \quad (14)$$

where \vec{c}_s and \vec{c}_p are such that $\vec{c}_i^\dagger S_{ii} \vec{c}_i = 1$, and

$$H'_p = H_{pp} + J_s + (K_s + H_{ps} \vec{c}_s \vec{c}_s^\dagger S_{sp} + S_{ps} \vec{c}_s \vec{c}_s^\dagger H_{sp}) \quad (15)$$

and

$$\epsilon_s = \vec{c}_i^\dagger H_{ii} \vec{c}_i. \quad (16)$$

Since $\vec{\chi}_s$ and $\vec{\chi}_p$ are of different symmetry, $S_{sp} = 0$ and Eqs. (13) and (14) simplify to

$$H'_s \vec{c}_s = \lambda_s S_{ss} \vec{c}_s \quad (17)$$

$$H'_p \vec{c}_p = \lambda_p S_{pp} \vec{c}_p \quad (18)$$

also

$$E = \lambda_s + \epsilon_p = \lambda_s + \lambda_p - \vec{c}_p^\dagger (J_s + K_s) \vec{c}_p \quad (19)$$

and

$$H'_p = H_{pp} + J_s + K_s \quad (20)$$

Now suppose the eigenvalues of Eq. (17) are

$\lambda_{s,1} \leq \lambda_{s,2} \leq \dots \leq \lambda_{s,N}$ with the corresponding eigenvectors $\vec{c}_{s,1}, \vec{c}_{s,2}, \dots, \vec{c}_{s,N}$ and similarly for Eq. (18).

Davidson points out that any of the $\vec{c}_{s,i}$, say $\vec{c}_{s,\alpha}$ can be used to form H'_p and any of the $\vec{c}_{p,i}$, say $\vec{c}_{p,\beta}$ can be used to form H'_s and hence at self-consistency Eqs. (17)

and (18) will be self-consistent with respect to $\vec{c}_{s,\alpha}(\alpha,\beta)$ and $\vec{c}_{p,\beta}(\alpha,\beta)$. Davidson proves that

$$\langle \phi_k | H | \phi_j \rangle = \delta_{kj} \quad (21)$$

where

$$\phi_k = 1/\sqrt{2} [\phi_s(1)\phi_{p,k}(2) \pm \phi_{p,k}(1)\phi_s(2)]$$

and

$$\phi_s = \vec{c}_s^\dagger(1,\beta)\vec{\chi}_s, \quad \phi_{p,k} = \vec{c}_{p,k}^\dagger(1,\beta)\vec{\chi}_p.$$

Hence the configurations are orthogonal and non-inter-acting. By using the method of MacDonald (34) which gives upper bounds to eigenvalues from the solution of the secular equation when the wave function is expanded in a truncated set of complete functions, one may write

$$\epsilon_s(1,\beta) + \lambda_{p,\beta}(1,\beta) \geq E_\beta \quad (22)$$

where E_β is the true β^{th} eigenvalue of H . Thus one is provided with a variational principle for excited states in this simple case which insures an upper bound to the true eigenvalue. This method provides a convenient comparison between upper bounds calculated by an ordinary variational treatment and the bounds calculated by the method proposed in this thesis.

The method just outlined provides the means of obtaining the values listed in Table 4 in the fifth and sixth columns. The values in the fifth column were

obtained by direct application of Davidson's method using the basis sets described above and optimizing the n 's. The wave functions corresponding to these energies are given in Tables 5 and 6. It should be noted that some of the vectors given in Tables 5 and 6 as well as some of those in Tables 2 and 3 have coefficients which are greater than unity. These vectors are, however, normalized, as they must be; the reason for the strange coefficients is the form of the functions chosen, i.e., all the basis functions of the same symmetry have a common n . Usually each basis function has its own orbital exponent which is optimized and the coefficients then are all close to or less than unity.

The sixth column of Table 4 contains the results obtained by Davidson using larger basis sets; these results should be close to the Hartree-Fock limit.

It should be noted that the bounds calculated give quite good limits on the true eigenvalues. The difference between the upper and lower bound values being, in the worst cases, only .005 a.u. (~3 kcal.). For the lowest states of a given symmetry the Upper Bound value and the $E_{\text{variational}}$ value are identical, since the upper bound equation reduces to the ordinary variational principle in these cases.

The fact that the upper bounds given by the Davidson method ($E_{\text{variational}}$ of Table 4) are better

Table 5

Singlet State Upper Bound Wave Functions - Davidson's Method

ϕ_s			ϕ_p		
n	η	c_n	n	η	c_n
$^1P \ 1s2p \ (A)$					
1	1.64	1.34383	2	0.624	0.46829
2	1.64	-0.50259	3	0.624	0.48996
3	1.64	0.14015	4	0.624	-0.03214
4	1.64	-0.02830	5	0.624	0.12795
$^1P \ 1s3p \ (A)$					
1	1.80	1.17168	2	0.355	-1.25864
2	1.80	-0.22546	3	0.355	1.13821
3	1.80	0.03362	4	0.355	0.76193
4	1.80	-0.00449	5	0.355	-0.03427
$^1P \ 1s4p \ (A)$					
1	1.88	1.10042	2	0.257	1.97148
2	1.88	-0.12536	3	0.257	-4.84864
3	1.88	0.01121	4	0.257	2.61793
4	1.88	-0.00113	5	0.257	0.96264

Table 6

Triplet State Upper Bound Wave Functions - Davidson's Method

ϕ_s			ϕ_p		
n	η	c_n	n	η	c_n
$^3P \ 1s2p \ (A)$					
1	1.76	1.20304	2	0.710	0.68640
2	1.76	-0.27858	3	0.710	-0.10798
3	1.76	0.05158	4	0.710	0.50040
4	1.76	0.00094	5	0.710	0.00028
$^3P \ 1s3p \ (A)$					
1	1.79	1.17834	2	0.437	-1.17537
2	1.79	-0.23779	3	0.437	1.42767
3	1.79	0.03893	4	0.437	-0.79388
4	1.79	-0.00328	5	0.437	1.17645
$^3P \ 1s4p \ (A)$					
1	1.85	1.12427	2	0.257	2.28960
2	1.85	-0.15873	3	0.257	-6.40743
3	1.85	0.01798	4	0.257	5.01656
4	1.85	-0.00101	5	0.257	-0.21458

than those of the method proposed in this thesis for the $^1P(1s3p)$ and $^3P(1s3p)$ states is explained by a simple argument. In the special case treated by Davidson, his method is equivalent to a variational principle which determines the function which gives a stationary value to E , i.e., it satisfies the equation, $\delta E = 0$. This is the same form as the ground state variational principle and it is only because of the nature of the trial functions chosen and the form of the problem which allows this equation to be valid for the determination of excited state functions also. As was shown previously the method proposed here gives an equation of the form $\delta E + \omega \delta \Delta = 0$.

The latter equation may be considered as a constrained variational problem with the former being the unconstrained problem. These problems are well known and it is a fact that the constrained problem cannot have a minimum which is as low as the minimum for the unconstrained problem. Hence Davidson's values are better upper bounds. However in the general case, when Davidson's method is not applicable, the other method is still valid and will yield values for an upper bound which would be otherwise unavailable.

III.4 He Excited State Wave Functions by ϵ^2/Δ Method

In section I.3 a method was proposed for the

determination of an approximate wave function for excited states which has the maximum overlap with the true eigenfunction. The method is based on the minimization of ϵ^2/Δ as described. In Chapter II the method was developed in terms of orbital theory and it is that formalism which can be directly applied here to yield the excited state wave function. The calculations were carried out for four states of He: $^1P(1s2p)$, $^1P(1s3p)$, $^3P(1s2p)$ and $^3P(1s3p)$ states. The basis set used is the same as that used for the calculations described in the last section.

For these calculations one should know the W_k in order to calculate ϵ . In all cases considered here the W_k were approximated by using the experimental energies of the appropriate states. It should be pointed out that if one did not know the W_k or have any experimental information that a double minimization procedure could be devised to obtain the best approximation to W_k automatically. That is, one could find the minimum of ϵ^2/Δ for a series of values of W_k , then considering the minimum values as a function of W_k one would choose the smallest of these minimum values and thus obtain the wave function and an approximation to the corresponding W_k .

In Table 7 the wave functions determined by the

Table 7

Excited State Wave Functions - ϵ^2/Δ Minimization Method

ϕ_s			ϕ_p		
n	η	c_n	n	η	c_n
$^1P \ 1s2p \ (B)$					
1	2.25	0.83850	2	0.668	0.41858
2	2.25	0.16110	3	0.668	0.44990
3	2.25	0.02780	4	0.668	0.02159
4	2.25	-0.00146	5	0.668	0.17857
$^3P \ 1s2p \ (B)$					
1	1.86	1.11008	2	0.700	0.71746
2	1.86	-0.14467	3	0.700	-0.10578
3	1.86	0.01676	4	0.700	0.46560
4	1.86	0.00726	5	0.700	-0.00067
$^1P \ 1s3p \ (B)$					
1	1.68	1.29512	2	0.354	-1.31116
2	1.68	-0.42127	3	0.354	1.29494
3	1.68	0.10502	4	0.354	0.62949
4	1.68	-0.01848	5	0.354	-0.00507
$^3P \ 1s3p \ (B)$					
1	2.45	0.73860	2	0.436	-1.20234
2	2.45	0.23844	3	0.436	1.48308
3	2.45	0.03785	4	0.436	-0.78487
4	2.45	0.03638	5	0.436	1.14108

ϵ^2/Δ minimization method are presented. The arguments presented in Chapter I for this method maintained that the functions obtained by this method should be the best overall wave function. This is investigated in the next section by calculating some expectation values of operators important in physical properties.

III.5 Calculation of Some Expectation Values

In order to demonstrate the validity of the thesis that the wave functions obtained by the minimization of ϵ^2/Δ should be the best functions over the whole of configuration space, some expectation values have been calculated for these functions.

If the trial function is designated as Φ , the expectation values calculated are given as

$$E = \langle \Phi | H | \Phi \rangle \quad (23)$$

$$\langle 1/r \rangle = \frac{1}{2} \langle \Phi | \sum_{i=1}^2 1/r_i | \Phi \rangle \quad (24)$$

$$\langle r \rangle = \frac{1}{2} \langle \Phi | \sum_{i=1}^2 r_i | \Phi \rangle \quad (25)$$

$$\langle r^2 \rangle = \frac{1}{2} \langle \Phi | \sum_{i=1}^2 r_i^2 | \Phi \rangle \quad (26)$$

where r_i is the distance of the i^{th} electron from the nucleus. In Table 8 a comparison is made of the expectation values calculated from the $^1P(1s2p)$ and

$^3P(1s3p)$ wave functions of Table 7 with the expectation values calculated from variational wave functions obtained by other methods. The other wave functions are those designated as:

- 1) B^L - the wave functions of Tables 2 and 3 which are there designated by (L) and described in detail in section III.3,
- 2) E - the appropriate wave functions of Tables 5 and 6 which are, in these cases of the lowest state of a given symmetry, equivalent to the wave functions determined by the ordinary variational principle.
- 3) "Exact" - the wave functions determined by Schiff et. al. (35) using 560 terms of a Pekeris type expansion. The latter are extremely accurate functions and for all practical purposes may be considered to be exact - hence the designation.

Comparing the values in the first three columns of Table 8 with those of the fourth column, it is readily seen that the ϵ^2/Δ wave functions give the best overall accuracy; indeed, the only value predicted better by the variational principle is that of the energy and the difference there is in the fifth decimal place.

A similar comparison is given for the $^1P(1s3p)$ and $^3P(1s3p)$ states of He in Table 9. For these states however the ordinary variational principle cannot be used and hence the method of Davidson described in the

Table 8

Comparison of Expectation Values Calculated from

Various Wave Functions: 1s2p

	<u>$^1P \ 1s2p$</u>			
	B^L	E	ϵ^2/Δ	"Exact"
-E	2.07204	2.12246	2.12243	2.12384
$\langle 1/r \rangle$	1.0457	1.1194	1.1229	1.12318
$\langle r \rangle$	6.134	2.9469	2.9223	2.91068
$\langle r^2 \rangle$	83.87	16.175	15.878	15.76565

	<u>$^3P \ 1s2p$</u>			
	B^L	E	ϵ^2/Δ	"Exact"
-E	2.07537	2.13134	2.13132	2.13316
$\langle 1/r \rangle$	1.0490	1.1309	1.1335	1.13324
$\langle r \rangle$	6.185	2.7004	2.6813	2.67396
$\langle r^2 \rangle$	75.54	13.417	13.245	13.21174

Table 9

Comparison of Expectation Values Calculated from

Various Wave Functions: 1s3p

1P 1s3p

	B^L	B^U	E	ϵ^2/Δ	"Exact"
-E	2.03844	2.07062	2.05473	2.05472	2.05515
$\langle 1/r \rangle$	1.0448	1.0229	1.0547	1.0528	1.05497
$\langle r \rangle$	6.122	12.055	6.720	6.695	6.67954
$\langle r^2 \rangle$	86.77	296.20	92.81	92.16	91.8727

3P 1s3p

	B^L	B^U	E	ϵ^2/Δ	"Exact"
-E	2.03999	2.07374	2.05750	2.05745	2.05808
$\langle 1/r \rangle$	1.0474	1.0239	1.0570	1.0597	1.05802
$\langle r \rangle$	6.302	11.574	6.364	6.332	6.32113
$\langle r^2 \rangle$	88.48	268.22	82.96	82.15	82.1098

last section applies to the determination of the wave functions in Tables 5 and 6. It is the appropriate wave functions of these tables that were used to calculate the expectation values given under the designation E in Table 9. The other designations of Table 9 have the same significance as in Table 8 with the addition that B^U denotes the results obtained from the appropriate wave functions given in Tables 2 and 3. Again the method involving the minimization of ϵ^2/Δ gives the best overall agreement with the "Exact" values of the operators considered.

Tables 8 and 9 demonstrate a rather important result: an approximate wave function is quite sensitive to the criterion which is used to determine it, and although it may predict the property very well which was used to judge its "goodness", other properties can be very inaccurate. This is particularly the case of the functions which give the upper and lower bound values. Although these functions give very good bounds, as shown in Table 4, they are practically useless for determining any other property. To a lesser degree the same criticism of the variational principle can be made; in trying to obtain the lowest possible value of E, a rather significant sacrifice is made in the wave function with respect to its ability to give reliable values for other properties.

The minimization of ϵ^2/Δ gives a general variational principle, which is applicable to the ground or excited states regardless of symmetry, for the determination of the best trial wave function ϕ .

III.6 Calculations of Lower Bound to He Ground State

As was mentioned at the end of Chapter I, there exist a few non-variational approaches to determining lower bounds of eigenvalues. Of these methods the one of Löwdin, which is based on perturbation theory, has received a great deal of attention. It is the purpose of this section to make a direct comparison between the method proposed in this thesis and the method of Löwdin, by considering the results of the two methods for the case of the ground state of the He atom.

The trial functions used for the method proposed here are of the general type

$$\phi = \sum_{\ell mn} C_{\ell mn} \chi_{\ell mn} \quad (27)$$

where the $C_{\ell mn}$ are coefficients to be determined by the variational calculation and will be such that ϕ gives the maximum value of the lower bound.

$$\chi_{\ell mn} = N_{\ell mn} s^{\ell} t^m u^n e^{-s/2} \quad (28)$$

where N_{mn} is a normalization factor, $s = k(r_1 + r_2)$, $t = k(r_2 - r_1)$ and $u = kr_{12}$, m is an even integer and

k is a scaling factor. The form of the Hamiltonian and all the necessary integrals are discussed in Appendix IV. For the calculations presented here the values of ϵ_{mn} taken in the summation for the three trial functions considered are presented in Table 10. The latter are also the same functions used for the "inner projection" space in the Löwdin method calculations presented here. A derivation of Löwdin's method is given in Appendix III and the necessary integrals are given in Appendix IV.

In Table 11 the results of the two methods are compared with the results of the Temple method for three basis sets. The basis functions listed in column one of Table 10 were used for the 6-function basis set. The functions of column two were added for the 10-function calculations and all of the functions shown to Table 10 were used for the 18-function calculations. In Table 11 the numbers in parentheses are the optimum values of the scaling factor k .

The results show that both the present method and Löwdin's method give a considerably better lower bound than does the usual Temple method. The difference between the present method and that of Löwdin for 18 basis functions is not very great and from the trend of Table 11 larger basis sets would probably give almost identical results. This is a rather important point since the present method can be extended to

Table 11
Comparison of Lower Bound Values

<u>Basis Functions</u>	<u>Present Method[†]</u>	<u>Lowdin Method*</u>	<u>Temple Method[†]</u>
6	-2.9147 (3.34)	-2.9098 (3.46)	-2.9260 (3.64)
10	-2.9080 (3.91)	-2.9060 (3.50)	-2.9132 (3.54)
18	-2.9041 (4.02)	-2.9039 (3.92)	-2.9055 (3.85)

† $E_1 = -2.1460$ was used as the lower bound to the true eigenvalue of the 2^1S state of He (37).

* $\mathcal{E} = -2.9037$ was used as the upper bound to the true eigenvalue of the 1^1S state of He (21).

handle many electron atoms without much difficulty, whereas Löwdin's method has the simple form (see Appendix III) discussed here only for two electron systems, since the perturbation term is simply $V = 1/r_{12}$. For many electron atoms the perturbation is much more complicated and the integrals which would arise as a result of this are quite intractable at present.

III.7 Summary and Conclusions

It has been shown here that it is possible to construct variational methods for the determination of upper and lower bounds, and for the determination of the best approximate wave function in the sense of the maximum overlap with the true eigenfunction. The results have shown that these methods are not only workable but that they yield quite good values.

For the bounds determined here, the associated wave functions have proved to be useless for the calculation of physical properties. In the Löwdin method for lower bounds the corresponding wave function cannot be written in a tractable form. However it would most certainly suffer from the same characteristic lack of utility, which seems to be the fate of wave functions associated with a bound value. Hence the variation method developed here for bounds is quite useful in determining bounds but

should not in any way be considered as a way to determine a valid approximation to an eigenfunction. The reason is that the bound formulations add contributions from other configurations to the trial wave functions which do not help in the description of the wave function associated with the state under consideration. This is most clearly seen in Löwdin's formulation for lower bounds, where contributions to the reference function are added from functions projected from another subspace. It is also true for the method proposed here. The validity of this statement can be attested to, numerically, by the wave functions presented here for the bounds. To obtain good bounds one must add in parts of function space which are not suited to the description of the eigenfunction. The ordinary variational principle is a special case of the bound method developed here. However it is a special case which fortunately does not suffer from the drawback just discussed. This is due to the fact that the function satisfies the equation $\delta E = 0$, rather than $\delta E + \omega \delta \Delta = 0$. It is the latter which is responsible for adding in the terms which are undesirable from the point of view of obtaining a good wave function; in particular, it is the quantity ω which is responsible. This can be seen by comparing the wave functions obtained by the bound method with those obtained by the ϵ^2/Δ method. In the former the ω is of such a form

that it adds in undesirable contributions, but in the latter the ω is of the correct form to obtain the best function. Although the ordinary variational method is thus a reasonable method for obtaining approximate wave functions, this is only of a secondary nature. The primary utility of the variational principle for lowest states should be recognized as a method for determining the best upper bound to the lowest state of a given symmetry.

For the determination of the best approximate wave function a variational method based on the minimization of ϵ^2/Δ has been developed. The resultant wave function has the maximum overlap with the true eigenfunction. Unlike the ordinary variational principle (which really gives the best upper bound for the ground state and not the best approximation to the eigenfunction), the method proposed here gives the wave function which has the least mean square deviation from the true eigenfunction over the whole of configuration space. The results on He indeed show that this method is superior to the ordinary variational principle for the determination of wave functions. It is furthermore general and can be used to determine an approximate wave function for any state.

In quantum chemistry one is not only interested in the energy of a system but also in calculating physical

and chemical properties. Since the method proposed here yields wave functions which are capable of giving values of physical properties which are superior to those of the ordinary variational method, it is hoped that this may constitute a contribution to the better prediction of phenomena of chemical interest.

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Appendix I

According to Eq. (2.2) E may be written as

$$E = \langle \Phi | \sum_{\pi} H_{\pi} + \frac{1}{2} \sum_{\sigma \neq \pi} 1/r_{\sigma\pi} | \Phi \rangle \quad (I.1)$$

Now considering each term separately one has

$$\sum_{\pi} \langle \Phi | H_{\pi} | \Phi \rangle = 2 \sum_{i\lambda\alpha} f_i^{\lambda} H_{ii}^{\lambda\alpha, \lambda\alpha} \quad (I.2)$$

and

$$\frac{1}{2} \sum_{\sigma \neq \pi} \langle \Phi | 1/r_{\sigma\pi} | \Phi \rangle = \sum_{i\lambda\alpha} \sum_{m\mu\beta} f_i^{\lambda} f_m^{\mu} N_{iimm}^{\lambda\alpha, \lambda\alpha, \mu\beta, \mu\beta} \quad (I.3)$$

The evaluation of the matrix components of the Hamiltonian with respect to Slater determinants, as given in the equations above, can be found in standard texts on quantum mechanics (23), however the notation here is quite different. The $\sum_{i\lambda\alpha}$ is to be interpreted in the following way. The function Φ consists of a set of orbitals

$$\{\phi_1^{\lambda\alpha}, \phi_2^{\lambda\alpha} \dots \phi_u^{\lambda\alpha}, \phi_1^{\mu\beta}, \phi_2^{\mu\beta} \dots \phi_v^{\mu\beta} \dots \phi_1^{\omega\epsilon}, \phi_2^{\omega\epsilon} \dots \phi_{\omega}^{\omega\epsilon}\}.$$

This set of orbitals may be decomposed into n subsets according to the symmetry species and subspecies of the orbitals, hence one has the group of subsets

$$\{\phi_1^{\lambda\alpha} \phi_2^{\lambda\alpha} \dots \phi_{d(\lambda\alpha)}^{\lambda\alpha}\}_1, \{\phi_1^{\mu\beta} \phi_2^{\mu\beta} \dots \phi_{d(\mu\beta)}^{\mu\beta}\}_2, \dots \{\phi_1^{\omega\epsilon} \phi_2^{\omega\epsilon} \dots \phi_{d(\omega\epsilon)}^{\omega\epsilon}\}_n$$

where $d(\lambda\alpha)$ is the dimension of the subspace spanned by the subset elements $\phi_i^{\lambda\alpha}$. The summation is then to be

carried out over all subsets and over all orbitals in a subset. This is obviously equivalent to a summation over all orbitals in the original set.

The following notation will also be introduced:

$$\sum_{i\lambda\alpha} \equiv \sum_{\vec{i}}. \quad \text{Thus}$$

$$\sum_{i\lambda\alpha} f_i^\lambda H_i^{\lambda\alpha} \equiv \sum_{\vec{i}} f_i^\lambda H_{\vec{i}}.$$

Note that the f_i^λ are not summed over the index α and hence the shorthand notation for f_i^λ cannot be used. In all such cases where the complete set of indices is not summed over the subset of indices which is summed over will be designated by explicitly affixing these indices to the quantities involved.

Using this new notation,

$$E = 2 \sum_{\vec{i}} f_i^\lambda H_{\vec{i}\vec{i}} + \sum_{\vec{i}\vec{m}} f_i^\lambda f_m^\mu N_{\vec{i}\vec{i}\vec{m}\vec{m}} \quad (\text{I.4})$$

where the $H_{\vec{i}\vec{i}}$ and $N_{\vec{i}\vec{i}\vec{m}\vec{m}}$ are as follows

$$H_{\vec{i}\vec{m}} = \langle \phi_{\vec{i}} | H | \phi_{\vec{m}} \rangle = \int \phi_{\vec{i}}^*(\rho) H_\rho \phi_{\vec{m}}(\rho) dV_\rho \quad (\text{I.5})$$

$$N_{\vec{i}\vec{m}\vec{n}\vec{p}} = 2 n_{\vec{i}\vec{m}\vec{n}\vec{p};1} N_{\uparrow;\vec{i}\vec{m}\vec{n}\vec{p}} - n_{\vec{i}\vec{m}\vec{n}\vec{p};2} N_{\downarrow;\vec{i}\vec{m}\vec{n}\vec{p}} \quad (\text{I.6})$$

where

$$N_{\uparrow;\vec{i}\vec{m}\vec{n}\vec{p}} = \langle \phi_{\vec{i}} | N_{\uparrow;\vec{n}\vec{p}} | \phi_{\vec{m}} \rangle = \iint \phi_{\vec{i}}^*(\rho) \phi_{\vec{m}}(\rho) [1/r_{\rho\tau}] \phi_{\vec{n}}^*(\tau) \phi_{\vec{p}}(\tau) dV_\rho dV_\tau \quad (\text{I.7})$$

and $N_{\downarrow; \vec{i} \vec{m} \vec{n} \vec{p}}$ is the exchange counterpart of (I.7), i. e., (I.7) with the electron labels of the second and fourth orbitals interchanged. The $n_{\vec{i} \vec{m} \vec{n} \vec{p}; 1}$ and $n_{\vec{i} \vec{m} \vec{n} \vec{p}; 2}$ are constants which depend upon the occupancies of the various orbitals involved and upon the multiplicity and orbital angular momentum of the multiplet under consideration.

Appendix II

From Eq. (2.5)

$$H^2 = \sum_{\pi\sigma} H_\pi H_\sigma + 2 \sum_{\pi} \sum_{\rho < \tau} \frac{H_\pi}{r_{\rho\tau}} + \sum_{\pi < \sigma} \sum_{\rho < \tau} \frac{1}{r_{\pi\sigma}} \frac{1}{r_{\rho\tau}} \quad (\text{II.1})$$

Now splitting the first and third terms into two new terms each,

$$\begin{aligned} H^2 = & \sum_{\pi} H_\pi^2 + \sum_{\sigma \neq \pi} H_\pi H_\sigma + 2 \sum_{\pi} \sum_{\rho < \tau} \frac{H_\pi}{r_{\rho\tau}} \\ & + \sum_{\pi < \sigma} \frac{1}{r_{\pi\sigma}^2} + \sum_{\substack{\pi < \sigma \\ \pi \neq \rho, \sigma \neq \tau}} \sum_{\rho < \tau} \frac{1}{r_{\pi\sigma}} \frac{1}{r_{\rho\tau}} \end{aligned} \quad (\text{II.2})$$

Now splitting up the third and fifth summations of (II.2) one obtains finally,

$$\begin{aligned} H^2 = & \sum_{\pi} H_\pi^2 + \sum_{\sigma \neq \pi} H_\pi H_\sigma + 2 \sum_{\pi < \tau} \frac{H_\pi}{r_{\pi\tau}} + 2 \sum_{\pi} \sum_{\substack{\rho < \tau \\ \rho \neq \pi}} \frac{H_\pi}{r_{\rho\tau}} \\ & + \sum_{\pi < \sigma} \frac{1}{r_{\pi\sigma}^2} + \sum_{\substack{\pi < \sigma \\ \pi \neq \tau}} \sum_{\sigma < \tau} \frac{1}{r_{\pi\sigma}} \frac{1}{r_{\sigma\tau}} + \sum_{\substack{\pi < \sigma \\ \pi \neq \rho, \sigma \neq \tau \\ \sigma \neq \rho}} \sum_{\rho < \tau} \frac{1}{r_{\pi\sigma}} \frac{1}{r_{\rho\tau}} \end{aligned} \quad (\text{II.3})$$

This arrangement of H^2 is more convenient for evaluating $\langle \Phi | H^2 | \Phi \rangle$ and obtaining unique terms. Each term of H^2 will now be evaluated with respect to Φ .

$$\sum_{\pi} \langle \Phi | H_\pi^2 | \Phi \rangle = \sum_{\vec{i}} f_i^\lambda X_{ii}^{\vec{i}\vec{i}} = \sum_{\vec{i}} f_i^\lambda X_i^{\vec{i}} \quad (\text{II.4})$$

$$\sum_{\sigma \neq \pi} \langle \Phi | H_{\pi} H_{\sigma} | \Phi \rangle = -2 \sum_{\substack{\vec{i} \vec{m} \\ i \neq m}} f_i^{\lambda} f_m^{\mu} H_{\vec{i} \vec{m}}^{\rightarrow \rightarrow} H_{\vec{m} \vec{i}}^{\rightarrow \rightarrow} + 2 \sum_{\vec{i} \vec{m}} f_i^{\lambda} f_m^{\mu} H_{\vec{i} \vec{i}}^{\rightarrow \rightarrow} H_{\vec{m} \vec{m}}^{\rightarrow \rightarrow} \quad (II.5)$$

$$2 \sum_{\pi < \tau} \langle \Phi | \frac{H_{\pi}}{r_{\pi \tau}} | \Phi \rangle = \sum_{\vec{i} \vec{m}} f_i^{\lambda} f_m^{\mu} P_{\vec{i} \vec{m}}^{\rightarrow \rightarrow} \quad (II.6)$$

$$\sum_{\pi < \sigma} \langle \Phi | \frac{1}{r_{\pi \sigma}} | \Phi \rangle = \sum_{\vec{i} \vec{m}} f_i^{\lambda} f_m^{\mu} Q_{\vec{i} \vec{m}}^{\rightarrow \rightarrow} \quad (II.7)$$

$$2 \sum_{\pi} \sum_{\substack{\rho < \tau \\ \rho \neq \pi}} \langle \Phi | \frac{H_{\pi}}{r_{\rho \tau}} | \Phi \rangle = - \sum_{\substack{\vec{i} \vec{m} \vec{n} \\ \vec{i} \neq \vec{m}}} f_i^{\lambda} f_m^{\mu} f_n^{\nu} H_{\vec{i} \vec{m}}^{\rightarrow \rightarrow} N_{\vec{m} \vec{i} \vec{n} \vec{n}}^{\rightarrow \rightarrow \rightarrow \rightarrow} \\ + 3 \sum_{\vec{i} \vec{m} \vec{n}} f_i^{\lambda} f_m^{\mu} f_n^{\nu} H_{\vec{i} \vec{i}}^{\rightarrow \rightarrow} N_{\vec{m} \vec{m} \vec{n} \vec{n}}^{\rightarrow \rightarrow \rightarrow \rightarrow} \quad (II.8)$$

$$\sum_{\pi < \sigma} \sum_{\substack{\sigma < \tau \\ \pi \neq \tau}} \langle \Phi | \frac{1}{r_{\pi \sigma}} \frac{1}{r_{\sigma \tau}} | \Phi \rangle = \sum_{\vec{i} \vec{m} \vec{n}} f_i^{\lambda} f_m^{\mu} f_n^{\nu} (T_{\vec{i} \vec{m} \vec{n}}^{\rightarrow \rightarrow \rightarrow} + Y_{\vec{i} \vec{m} \vec{n}}^{\rightarrow \rightarrow \rightarrow}) \quad (II.9)$$

$$\sum_{\substack{\pi < \sigma \\ \pi \neq \rho \\ \sigma \neq \rho}} \sum_{\substack{\rho < \tau \\ \sigma \neq \tau}} \langle \Phi | \frac{1}{r_{\pi \sigma}} \frac{1}{r_{\rho \tau}} | \Phi \rangle = - \sum_{\substack{\vec{i} \vec{m} \vec{n} \vec{p} \\ \vec{m} \neq \vec{n}}} f_i^{\lambda} f_m^{\mu} f_n^{\nu} f_p^{\zeta} N_{\vec{i} \vec{i} \vec{m} \vec{n}}^{\rightarrow \rightarrow \rightarrow \rightarrow} N_{\vec{n} \vec{m} \vec{p} \vec{p}}^{\rightarrow \rightarrow \rightarrow \rightarrow} \\ + \sum_{\vec{i} \vec{m} \vec{n} \vec{p}} \frac{1}{3} N_{\vec{i} \vec{m} \vec{n} \vec{p}}^{\rightarrow \rightarrow \rightarrow \rightarrow} [2 N_{\vec{p} \vec{m} \vec{n} \vec{i}}^{\rightarrow \rightarrow \rightarrow \rightarrow} + N_{\vec{n} \vec{m} \vec{p} \vec{i}}^{\rightarrow \rightarrow \rightarrow \rightarrow}] - \sum_{\vec{i} \vec{m} \vec{n} \vec{p}} N_{\vec{i} \vec{i} \vec{m} \vec{m}}^{\rightarrow \rightarrow \rightarrow \rightarrow} N_{\vec{n} \vec{n} \vec{p} \vec{p}}^{\rightarrow \rightarrow \rightarrow \rightarrow} \quad (II.10)$$

where $N_{\vec{i} \vec{m} \vec{n} \vec{p}}^{\rightarrow \rightarrow \rightarrow \rightarrow}$ and $H_{\vec{i} \vec{m}}^{\rightarrow \rightarrow}$ are as defined in Appendix I and where

$$P_{\vec{i} \vec{m}}^{\rightarrow \rightarrow} = 2 p_{\vec{i} \vec{m}; 1}^{\rightarrow \rightarrow} P_{\uparrow; \vec{i} \vec{m}}^{\rightarrow \rightarrow} - p_{\vec{i} \vec{m}; 2}^{\rightarrow \rightarrow} P_{\downarrow; \vec{i} \vec{m}}^{\rightarrow \rightarrow} \quad (II.11)$$

$$Q_{\vec{i} \vec{m}}^{\rightarrow \rightarrow} = 2 q_{\vec{i} \vec{m}; 1}^{\rightarrow \rightarrow} Q_{\uparrow; \vec{i} \vec{m}}^{\rightarrow \rightarrow} - q_{\vec{i} \vec{m}; 2}^{\rightarrow \rightarrow} Q_{\downarrow; \vec{i} \vec{m}}^{\rightarrow \rightarrow} \quad (II.12)$$

$$T_{\vec{i} \vec{m} \vec{n}}^{\rightarrow \rightarrow \rightarrow} = 2 t_{\vec{i} \vec{m} \vec{n}; 1}^{\rightarrow \rightarrow \rightarrow} T_{\uparrow; \vec{i} \vec{m} \vec{n}}^{\rightarrow \rightarrow \rightarrow} - t_{\vec{i} \vec{m} \vec{n}; 2}^{\rightarrow \rightarrow \rightarrow} T_{\downarrow; \vec{i} \vec{m} \vec{n}}^{\rightarrow \rightarrow \rightarrow} \quad (II.13)$$

$$Y_{\vec{1}\vec{m}\vec{n}}^{\vec{\uparrow}\vec{\uparrow}\vec{\uparrow}} = 2y_{\vec{1}\vec{m}\vec{n};1}^{\vec{\uparrow}\vec{\uparrow}\vec{\uparrow}} Y_{\vec{\uparrow};\vec{1}\vec{m}\vec{n}}^{\vec{\uparrow}\vec{\uparrow}\vec{\uparrow}} - y_{\vec{1}\vec{m}\vec{n};2}^{\vec{\uparrow}\vec{\uparrow}\vec{\uparrow}} Y_{\vec{\downarrow};\vec{1}\vec{m}\vec{n}}^{\vec{\uparrow}\vec{\uparrow}\vec{\uparrow}} \quad (\text{II.14})$$

The explicit forms of the integrals involved in the above expressions are given below.

$$X_{\vec{1}\vec{m}}^{\vec{\uparrow}\vec{\uparrow}} = \int [H^{\dagger} \phi_{\vec{1}}^*(\rho)] [H \phi_{\vec{m}}^{\vec{\uparrow}}(\rho)] dV_{\rho} \quad (\text{II.15})$$

$$P_{\vec{\uparrow};\vec{1}\vec{m}}^{\vec{\uparrow}\vec{\uparrow}} = \iint \phi_{\vec{1}}^*(\rho) \phi_{\vec{1}}^{\vec{\uparrow}}(\rho) \left(\frac{1}{r_{\rho\tau}}\right) \phi_{\vec{m}}^*(\tau) [H \phi_{\vec{m}}^{\vec{\uparrow}}(\tau)] dV_{\rho} dV_{\tau} \quad (\text{II.16})$$

$$Q_{\vec{\uparrow};\vec{1}\vec{m}}^{\vec{\uparrow}\vec{\uparrow}} = \iint \phi_{\vec{1}}^*(\rho) \phi_{\vec{1}}^{\vec{\uparrow}}(\rho) \left(\frac{1}{r_{\rho\tau}}\right)^2 \phi_{\vec{m}}^*(\tau) \phi_{\vec{m}}^{\vec{\uparrow}}(\tau) dV_{\rho} dV_{\tau} \quad (\text{II.17})$$

$$\begin{aligned} T_{\vec{\uparrow};\vec{1}\vec{m}\vec{n}}^{\vec{\uparrow}\vec{\uparrow}\vec{\uparrow}} &= \iiint \phi_{\vec{1}}^*(\rho) \phi_{\vec{1}}^{\vec{\uparrow}}(\rho) \left(\frac{1}{r_{\rho\tau}}\right) \phi_{\vec{m}}^*(\tau) \phi_{\vec{m}}^{\vec{\uparrow}}(\tau) \left(\frac{1}{r_{\rho\eta}}\right) \\ &\times \phi_{\vec{n}}^*(\eta) \phi_{\vec{n}}^{\vec{\uparrow}}(\eta) dV_{\rho} dV_{\tau} dV_{\eta} \end{aligned} \quad (\text{II.18})$$

$$\begin{aligned} Y_{\vec{\uparrow};\vec{1}\vec{m}\vec{n}}^{\vec{\uparrow}\vec{\uparrow}\vec{\uparrow}} &= \iiint \phi_{\vec{1}}^*(\rho) \phi_{\vec{m}}^{\vec{\uparrow}}(\rho) \left(\frac{1}{r_{\rho\tau}}\right) \phi_{\vec{m}}^*(\tau) \phi_{\vec{1}}^{\vec{\uparrow}}(\tau) \left(\frac{1}{r_{\rho\eta}}\right) \\ &\times \phi_{\vec{n}}^*(\eta) \phi_{\vec{n}}^{\vec{\uparrow}}(\eta) dV_{\rho} dV_{\tau} dV_{\eta} \end{aligned} \quad (\text{II.19})$$

the integrals $P_{\vec{\downarrow};\vec{1}\vec{m}}^{\vec{\uparrow}\vec{\uparrow}}$, $Q_{\vec{\downarrow};\vec{1}\vec{m}}^{\vec{\uparrow}\vec{\uparrow}}$, $T_{\vec{\downarrow};\vec{1}\vec{m}\vec{n}}^{\vec{\uparrow}\vec{\uparrow}\vec{\uparrow}}$ and $Y_{\vec{\downarrow};\vec{1}\vec{m}\vec{n}}^{\vec{\uparrow}\vec{\uparrow}\vec{\uparrow}}$ are the exchange counterparts of the above integrals. The exchange integrals to the first two are given by interchanging the electron labels of the second and fourth orbitals. For the second two cases the integrals are obtained by interchanging the electron labels of the fourth and sixth orbitals.

The coefficients appearing in Eqs. (II.11) to (II.14) are constants depending on the occupancies of the orbitals

involved and on the multiplicity and orbital angular momentum of the multiplet under consideration.

$\langle \Phi | H^2 | \Phi \rangle$ may now be written as

$$\begin{aligned}
 \langle H^2 \rangle = & 2 \sum_i f_i^\lambda X_i^\lambda - 2 \sum_{\substack{\vec{i}\vec{m} \\ \vec{i} \neq \vec{m}}} f_i^\lambda f_m^\mu H_{\vec{i}\vec{m}}^{\lambda\mu} H_{\vec{m}\vec{i}}^{\mu\lambda} + 2 \sum_{\vec{i}\vec{m}} f_i^\lambda f_m^\mu H_{\vec{i}\vec{i}}^{\lambda\lambda} H_{\vec{m}\vec{m}}^{\mu\mu} \\
 & + \sum_{\vec{i}\vec{m}} f_i^\lambda f_m^\mu (P_{\vec{i}\vec{m}}^{\lambda\mu} + Q_{\vec{i}\vec{m}}^{\lambda\mu}) - \sum_{\substack{\vec{i}\vec{m}\vec{n} \\ \vec{i} \neq \vec{m}}} f_i^\lambda f_m^\mu f_n^\nu H_{\vec{i}\vec{m}}^{\lambda\mu} N_{\vec{m}\vec{i}\vec{n}\vec{n}}^{\mu\nu} \\
 & + \sum_{\vec{i}\vec{m}\vec{n}} f_i^\lambda f_m^\mu f_n^\nu (3H_{\vec{i}\vec{i}}^{\lambda\lambda} N_{\vec{m}\vec{m}\vec{n}\vec{n}}^{\mu\nu} + T_{\vec{i}\vec{m}\vec{n}}^{\lambda\mu\nu} + Y_{\vec{i}\vec{m}\vec{n}}^{\lambda\mu\nu}) \\
 & - \sum_{\substack{\vec{i}\vec{m}\vec{n}\vec{p} \\ \vec{m} \neq \vec{n}}} f_i^\lambda f_m^\mu f_n^\nu f_p^\zeta (2N_{\vec{i}\vec{i}\vec{m}\vec{n}}^{\lambda\mu\nu} N_{\vec{n}\vec{m}\vec{p}\vec{p}}^{\mu\nu\zeta}) \\
 & - \sum_{\vec{i}\vec{m}\vec{n}\vec{p}} f_i^\lambda f_m^\mu f_n^\nu f_p^\zeta \{ N_{\vec{i}\vec{i}\vec{m}\vec{m}}^{\lambda\lambda\mu\mu} N_{\vec{n}\vec{n}\vec{p}\vec{p}}^{\nu\nu\zeta\zeta} - (\frac{1}{3} N_{\vec{i}\vec{m}\vec{n}\vec{p}}^{\lambda\mu\nu\zeta} [2N_{\vec{p}\vec{m}\vec{n}\vec{i}}^{\mu\nu\zeta\lambda} + N_{\vec{n}\vec{m}\vec{p}\vec{i}}^{\mu\nu\zeta\lambda}]) \}
 \end{aligned} \tag{II.20}$$

Since $\Delta = \langle H^2 \rangle - E^2$, E^2 must be subtracted from (II.20) in order to obtain the final result.

$$\begin{aligned}
 E^2 = & 4 \sum_{\vec{i}\vec{m}} f_i^\lambda f_m^\mu H_{\vec{i}\vec{i}}^{\lambda\lambda} H_{\vec{m}\vec{m}}^{\mu\mu} + 4 \sum_{\vec{i}\vec{m}\vec{n}} f_i^\lambda f_m^\mu f_n^\nu H_{\vec{i}\vec{i}}^{\lambda\lambda} N_{\vec{m}\vec{m}\vec{n}\vec{n}}^{\mu\nu} \\
 & + \sum_{\vec{i}\vec{m}\vec{n}\vec{p}} f_i^\lambda f_m^\mu f_n^\nu f_p^\zeta N_{\vec{i}\vec{i}\vec{m}\vec{m}}^{\lambda\lambda\mu\mu} N_{\vec{n}\vec{n}\vec{p}\vec{p}}^{\nu\nu\zeta\zeta}
 \end{aligned} \tag{II.21}$$

After subtraction of (II.21) from (II.20) one obtains, after rearranging terms,

$$\begin{aligned}
 \Delta = & 2 \sum_{\vec{i}} f_i^\lambda X_{\vec{i}} + \sum_{\vec{i}\vec{m}} f_i^\lambda f_m^\mu [P_{\vec{i}\vec{m}} + Q_{\vec{i}\vec{m}} - 2H_{\vec{i}\vec{m}} H_{\vec{m}\vec{i}}] + \sum_{\vec{i}\vec{m}\vec{n}} f_i^\lambda f_m^\mu f_n^\nu \\
 & \times [T_{\vec{i}\vec{m}\vec{n}} + Y_{\vec{i}\vec{m}\vec{n}} - H_{\vec{i}\vec{m}} N_{\vec{m}\vec{i}\vec{n}\vec{n}}] + \sum_{\vec{i}\vec{m}\vec{n}\vec{p}} f_i^\lambda f_m^\mu f_n^\nu f_p^\zeta \\
 & \times \left[\frac{1}{3} N_{\vec{i}\vec{m}\vec{n}\vec{p}} (2N_{\vec{p}\vec{m}\vec{n}\vec{i}} + N_{\vec{n}\vec{m}\vec{p}\vec{i}}) - 2N_{\vec{i}\vec{i}\vec{m}\vec{n}} N_{\vec{n}\vec{m}\vec{p}\vec{p}} \right] \quad (\text{II.22})
 \end{aligned}$$

If now the term in the first bracket is denoted as $A_{*,\vec{i}\vec{m}}$, the term in the second bracket as $B_{*,\vec{i}\vec{m}\vec{n}}$ and the one in the third as $C_{*,\vec{i}\vec{m}\vec{n}\vec{p}}$, then Δ may be written finally as

$$\begin{aligned}
 \Delta = & 2 \sum_{\vec{i}} f_i^\lambda X_{\vec{i}} + \sum_{\vec{i}\vec{m}} f_i^\lambda f_m^\mu A_{*,\vec{i}\vec{m}} + \sum_{\vec{i}\vec{m}\vec{n}} f_i^\lambda f_m^\mu f_n^\nu B_{*,\vec{i}\vec{m}\vec{n}} \\
 & + \sum_{\vec{i}\vec{m}\vec{n}\vec{p}} f_i^\lambda f_m^\mu f_n^\nu f_p^\zeta C_{*,\vec{i}\vec{m}\vec{n}\vec{p}} \quad (\text{II.23})
 \end{aligned}$$

If one now defines symmetrical operators with respect to subscripts and superscripts [see Appendix II of the paper by Fraga and Birss (29)] the form of Eq. (2.6) is finally obtained. It must be noted however that the coefficients in the linear combinations of integrals in (II.23) and Eq. (2.6) differ. This difference is explained, and the relationship between the two sets of coefficients is to be found, in the paper of Fraga and Birss.

Appendix III

In this Appendix Löwdin's method for determining lower bounds will be presented (19); his notation will be used throughout.

It is necessary in order to understand his final formula to outline its derivation here, even though it is somewhat lengthy. It starts with the partitioning of the secular equation in order to obtain a bracketing theorem for the eigenvalues; this provides a means of giving bounds to the eigenvalues. Then the method has to be developed in terms of an operator formalism so that perturbation theory may be applied and the reaction operator introduced. However the reaction operator contains an infinite expansion and therefore must be approximated in some manner. This is accomplished by a so-called inner projection technique. With this accomplished one may finally write his formula in its final form after a number of algebraic substitutions and manipulations.

Partitioning the Secular Equation

Consider the time independent Schrödinger equation

$$H\Psi = E\Psi \quad (\text{III.1})$$

where H is a Hermitian operator and Ψ is the exact wave function. Further, suppose E is the lowest eigenvalue and that it is discrete and non-degenerate. Then one may choose a complete orthonormal set, $\{\phi_k\}$, in order to express Ψ as

$$\Psi = \sum_k c_k \Phi_k \quad (\text{III.2})$$

Thus equation (III.1) may be rewritten in matrix notation as

$$\tilde{H} \vec{c} = E \vec{c} \quad (\text{III.3})$$

where

$$H_{kl} = \langle \Phi_k | H | \Phi_l \rangle.$$

One may write Eq. (III.3) then as

$$\tilde{M} \vec{c} = 0 \quad (\text{III.4})$$

where

$$\tilde{M} = \tilde{H} - E \cdot \underline{1}.$$

Now suppose that the basis $\Phi = \{\Phi_k\}$ is divided into two sets, $\vec{\Phi}_a$ and $\vec{\Phi}_b$. Then \tilde{M} and \vec{c} will become

$$\tilde{M} = \begin{pmatrix} \tilde{M}_{aa} & \tilde{M}_{ab} \\ \tilde{M}_{ba} & \tilde{M}_{bb} \end{pmatrix}, \quad \vec{c} = \begin{pmatrix} \vec{c}_a \\ \vec{c}_b \end{pmatrix}. \quad (\text{III.5})$$

Hence Eq. (III.4) may be written as

$$\begin{aligned} \tilde{M}_{aa} \vec{c}_a + \tilde{M}_{ab} \vec{c}_b &= 0 \\ \tilde{M}_{ba} \vec{c}_a + \tilde{M}_{bb} \vec{c}_b &= 0. \end{aligned} \quad (\text{III.6})$$

If one solves for \vec{c}_b from the second of the equations (III.6), then

$$\vec{c}_b = -\tilde{M}_{bb}^{-1} \tilde{M}_{ba} \vec{c}_a. \quad (\text{III.7})$$

This equation of course is valid only if the matrix \tilde{M}_{bb} has an inverse. Combining Eq. (III.7) with the first of the equations (III.6), one obtains

$$(\tilde{M}_{aa} - \tilde{M}_{ab} \tilde{M}_{bb}^{-1} \tilde{M}_{ba}) \vec{c}_a = 0. \quad (\text{III.8})$$

Now recalling that $\tilde{M} = \tilde{H} - E \cdot \tilde{1}$ one may rewrite Eq. (III.3) by the use of Eq. (III.8) as

$$[\tilde{H}_{aa} + \tilde{H}_{ab}(E \cdot \tilde{1}_{bb} - \tilde{H}_{bb})^{-1} \tilde{H}_{ba}] \vec{c}_a = E \vec{c}_a \quad (\text{III.9})$$

The subspaces a and b may in general be chosen arbitrarily, but for the present application the choice of $\vec{\phi}_a = \phi_1$, i. e., a one dimensional subspace for a, will be made. With this choice Eq. (III.9) becomes, for $c_1 \neq 0$

$$E = H_{11} + H_{1b}(E \cdot \tilde{1}_{bb} - H_{bb})^{-1} H_{b1}. \quad (\text{III.10})$$

Since this gives an implicit expression for the energy, E, Löwdin defines a function $\epsilon_1 = f(\epsilon)$ given explicitly as

$$\epsilon_1 = H_{11} + H_{1b}(\epsilon \cdot \tilde{1}_{bb} - H_{bb})^{-1} H_{b1} \equiv f(\epsilon) \quad (\text{III.11})$$

Equation (III.10) is reproduced by Equation (III.11) when $\epsilon_1 = \epsilon = E$. Equation (III.11) may then be used to obtain a "bracketing theorem" for the quantities ϵ and ϵ_1 .

The Bracketing Theorem

One obtains from Eq. (III.11)

$$\frac{d\epsilon_1}{d\epsilon} = -H_{1b}(\epsilon \cdot \tilde{1}_{bb} - H_{bb})^{-2} H_{b1}, \quad (\text{III.12})$$

and from Eq. (III.7) one has

$$\vec{c}_b = (\epsilon \cdot \tilde{1}_{bb} - H_{bb})^{-1} H_{b1} c_1. \quad (\text{III.13})$$

Combining Eqs. (III.12) and (III.13) one obtains

$$\frac{d\epsilon_1}{d\epsilon} = - \frac{\vec{c}_b^\dagger \vec{c}_b}{c_1^* c_1}. \quad (\text{III.14})$$

Now, if $\mathcal{E}_1 = E + \varepsilon_1$ and $\mathcal{E} = E + \varepsilon$ and since $E = f(E)$ one obtains by use of Lagrange's mean value theorem

$$E + \varepsilon_1 = f(E + \varepsilon) = f(E) + \varepsilon f'(E + \theta\varepsilon) \quad (\text{III.15})$$

hence

$$\varepsilon_1 = \varepsilon f'(E + \theta\varepsilon) = \varepsilon \frac{d\mathcal{E}_1}{d\mathcal{E}} = \frac{\varepsilon df(E + \theta\varepsilon)}{d\mathcal{E}} \quad (\text{III.16})$$

where $0 \leq \theta \leq 1$. Now $f'(E + \theta\varepsilon)$ must be a negative quantity as a result of Eq. (III.14), hence ε_1 and ε must have opposite signs and thus \mathcal{E}_1 and \mathcal{E} must "bracket" at least one true eigenvalue.

The Operator Formalism

In order to proceed it is necessary to write Eq. (III.11) in operator form. To this end consider the projection operator O and an arbitrary trial function ϕ , such that

$$O\phi = \phi \quad (\text{III.17})$$

where ϕ is the reference function which spans the one dimensional subspace a , i. e., let $\phi_1 = \phi$. Let the operator P be defined as

$$P = 1 - O, \quad OP = 0 \quad (\text{III.18})$$

where 1 is the identity operator. Then $(E \cdot 1_{bb} - H_{bb})^{-1}$ may be considered as the matrix representation, in the basis $\{\phi_k\}$, of the operator

$$T = P[\alpha \cdot O + P(E - H)P]^{-1} P \quad (\text{III.19})$$

where $\alpha \neq 0$ is an arbitrary number. The need for defining

the operator T in such a manner arises from the fact that $(E \cdot \underline{1}_{bb} - H_{bb})^{-1}$ is the inverse of the corner of a matrix and it must be insured that this inverse properly exists. With the definition of T given above this will be the case. Now by defining an operator

$$\Omega = O + THO \quad (III.20)$$

such that $H\Omega = E\Omega \quad \Omega^2 = \Omega \quad \text{and} \quad \text{Tr}(\Omega) = 1 \quad (III.21)$

one obtains $\Psi = \Omega\phi = \phi + TH\phi \quad (III.22)$

since $H\Psi = H\Omega\phi = E\Omega\phi = E\Psi. \quad (III.23)$

In the above it is assumed that $\langle\phi|O|\phi\rangle = 1$. Note that

$$\begin{aligned} (H - E)\Omega &= (O + P)(H - E)\Omega \\ &= O(H - E)\Omega = O(H - E)(O + THO) \\ &= O(H + HTH - E)O = 0 \end{aligned}$$

which gives $OEO = O(H + HTH)O \quad (III.24)$

If this equation is multiplied on the right by ϕ and on the left by ϕ^* and integrated, one obtains

$$E = \langle\phi|H + HTH|\phi\rangle. \quad (III.25)$$

Hence one may finally rewrite Eq. (III.11) in operator form

as $\epsilon_1 = \langle\phi|H + H \frac{P}{\epsilon - H} H|\phi\rangle \equiv f(\epsilon). \quad (III.26)$

Introduction of the Reaction Operator

Löwdin now chooses to express the Hamiltonian as

$$H = H_0 + V \quad (\text{III.27})$$

where H_0 is the unperturbed Hamiltonian and V is the perturbation and the reference function ϕ is chosen to be ϕ_0 , then with

$$\begin{aligned} H_0 \phi_0 &= E_0 \phi_0 \\ 0 &= |\phi_0\rangle \langle \phi_0| \end{aligned} \quad (\text{III.28})$$

one obtains

$$TH\phi = TH\phi_0 = T(H_0 + V)\phi_0 = T(E_0 + V)\phi_0 = TV\phi_0. \quad (\text{III.29})$$

Hence Eq. (III.22) becomes

$$\Psi_{\xi} = \phi_0 + TH\phi_0 = (1 + TV)\phi_0 \quad (\text{III.30})$$

and Eq. (III.26) becomes

$$\xi_1 = \langle \phi_0 | H + HTH | \phi_0 \rangle = E_0 + \langle \phi_0 | V + VTV | \phi_0 \rangle, \quad (\text{III.31})$$

and $t = V + VTV$ is called the "reaction operator". Thus Eq. (III.31) may be rewritten as

$$\xi_1 = E_0 + \langle \phi_0 | t | \phi_0 \rangle. \quad (\text{III.32})$$

Since

$$T = P[\alpha \cdot 0 + P(\xi - H)P]^{-1}P = P[\alpha \cdot 0 + P(\xi - H_0)P - PVP]^{-1}P \quad (\text{III.33})$$

if one designates $P[\alpha \cdot 0 + P(\xi - H_0)P]^{-1}P$ as T_0 ,

$[\alpha \cdot 0 + P(\xi - H_0)P]$ as A and $[PVP]$ as B , one will obtain the following

$$T = T_0 + T_0VT = T_0(1 + VT) \quad (\text{III.34})$$

by use of the identity

$$(A - B)^{-1} \equiv A^{-1} + A^{-1}B(A - B)^{-1}. \quad (\text{III.35})$$

Multiplying Eq. (III.34) on the right by V , one obtains

$$TV = T_o(V + VTV) = T_o t$$

and now multiplying on the left by V and adding V to each side of the equation

$$V + VTV = V + VT_o t$$

or

$$t = V + VT_o t \quad (\text{III.36})$$

From Eq. (III.36) one obtains

$$t - VT_o t = (1 - VT_o)t = V$$

and dividing both sides by V one obtains

$$1 = (V^{-1} - T_o)t,$$

provided V^{-1} exists, Hence one may finally write

$$t = (V^{-1} - T_o)^{-1}. \quad (\text{III.37})$$

However T_o involves an infinite expansion in terms of the unperturbed eigenfunctions and thus t cannot be determined explicitly. Hence one must try to approximate t in some manner. To do this the idea of an "inner projection" is needed.

The inner projection of t .

Suppose A is a self-adjoint positive-definite operator, then one may write

$$A = \sum_k a_k |U_k\rangle \langle U_k| \quad (\text{III.38})$$

where a_k and U_k are the eigenvalues and eigenfunctions of the operator A , and $a_k > 0$. One may now define the positive square root of A as

$$A^{1/2} = \sum_k a_k^{1/2} |U_k\rangle \langle U_k|. \quad (\text{III.39})$$

Now using the projection operator, O , one may define an "inner projection", A' , as

$$A' = A^{1/2} O A^{1/2}, \quad (\text{III.40})$$

where

$$O = \tilde{f} \Delta^{-1} f^\dagger = \sum_{k1} |f_k\rangle \Delta_{k1}^{-1} \langle f_1| \quad (\text{III.41})$$

for a set of linearly independent elements $\{f_i\}$, and $\Delta_{k1} = \langle f_k | f_1 \rangle_{k1}$. The inner projection is such that it satisfies the inequality

$$0 < A' < A. \quad (\text{III.42})$$

Thus if t is a positive definite operator

$$t' = t^{1/2} \tilde{f} \Delta^{-1} f^\dagger t^{1/2} < t \quad (\text{III.43})$$

and hence

$$E_0 + \langle \phi_0 | t | \phi_0 \rangle > E_0 + \langle \phi_0 | t' | \phi_0 \rangle. \quad (\text{III.44})$$

Thus t' will provide a lower bound to t and $\epsilon_1 = E_0 + \langle \phi_0 | t' | \phi_0 \rangle$ will provide a lower bound to the true eigenvalues. If one substitutes $h = t^{1/2} \tilde{f}$ into Eq. (III.43) one obtains

$$t' = \tilde{h} \Delta^{-1} h^\dagger, \quad \Delta = \tilde{h}^\dagger t^{-1} h. \quad (\text{III.45})$$

Löwdin then chooses the substitution $h = (\epsilon - H_0)_j^\dagger$, which gives

$$\langle \phi_0 | t' | \phi_0 \rangle = (\mathcal{E} - E_0)^2 \langle \phi_0 | \vec{j} \rangle \Delta^{-1} \langle \vec{j} | \phi_0 \rangle, \quad (\text{III.46})$$

where $\vec{j} = (j_1, j_2, \dots, j_n)$ is an arbitrary function space and where Δ^{-1} is the inverse of the following nth order matrix:

$$\begin{aligned} \Delta = \langle \vec{j} | (\mathcal{E} - H_0) V^{-1} (\mathcal{E} - H_0) | \vec{j} \rangle - \langle \vec{j} | \mathcal{E} - H_0 | \vec{j} \rangle \\ + (\mathcal{E} - E_0) \langle \vec{j} | \phi_0 \rangle \langle \phi_0 | \vec{j} \rangle. \end{aligned} \quad (\text{III.47})$$

Application to the Ground State

For the case of the application to the ground state $V^{-1} = r_{12}$ and Eq. (III.47) may be rewritten as

$$\begin{aligned} \Delta = \mathcal{E}^2 \langle \vec{j} | r_{12} | \vec{j} \rangle - \mathcal{E} \langle \vec{j} | H_0 r_{12} | \vec{j} \rangle - \mathcal{E} \langle \vec{j} | r_{12} H_0 | \vec{j} \rangle + \langle \vec{j} | H_0 r_{12} H_0 | \vec{j} \rangle \\ - \mathcal{E} \langle \vec{j} | \vec{j} \rangle + \langle \vec{j} | H_0 | \vec{j} \rangle + (\mathcal{E} - E_0) \langle \vec{j} | \phi_0 \rangle \langle \phi_0 | \vec{j} \rangle \end{aligned} \quad (\text{III.48})$$

where the $\{j_k\}$ are of the Hylleraas type, i. e.,

$$\{j_k\} = \{x_{1mn}\} = \{N_{1mn} s^1 t^m u^n e^{-s/2}\}. \quad (\text{III.49})$$

The evaluation of the integrals in Eq. (III.48) using the functions of Eq. (III.49) is discussed in Appendix IV.

In order to carry out a calculation of this type, one must first compute the matrix Δ , then find its inverse, Δ^{-1} , one must then carry out the multiplication of Eq. (III.46) and finally add the latter quantity to the unperturbed energy in order to obtain the lower bound \mathcal{E}_1 .

Appendix IV

In this Appendix the explicit forms of the integrals needed in the application of the method proposed in this thesis and in the application of Löwdin's method to the groundstate of He will be presented. These integrals are evaluated by a modification of the analysis of Wilets and Cherry (36).

The functions used in these calculations are of the Hylleraas type and are given by

$$\chi_{lmn} = N_{lmn} s^l t^m u^n e^{-s/2} \quad (\text{IV.1})$$

where $s = k(r_1 + r_2)$, $t = k(r_2 - r_1)$ and $u = kr_{12}$; m is always an even integer. It is convenient for what follows to define the following functions

$$\begin{aligned} A(p, q, r) &= \frac{2\pi^2}{k^6} \int_0^\infty e^{-s} s^p ds \int_0^s u^r du \int_0^u t^q (s^2 - t^2) dt \\ &= B(p + 2, q, r) - B(p, q + 2, r) \end{aligned} \quad (\text{IV.2})$$

$$\begin{aligned} B(p, q, r) &= \frac{2\pi^2}{k^6} \int_0^\infty e^{-s} s^p ds \int_0^s u^r du \int_0^u t^q dt \\ &= \frac{2\pi^2}{(q + 1)k^6} \int_0^\infty e^{-s} s^p ds \int_0^s u^{q + r + 1} du \\ &= \frac{2\pi^2}{(q + 1)(q + r + 2)k^6} \int_0^\infty e^{-s} s^{p + q + r + 2} ds \\ &= \frac{2\pi^2 (p + q + r + 2)!}{k^6 (q + 1)(q + r + 2)} \end{aligned} \quad (\text{IV.3})$$

$$C(p, q, r) = \frac{2\pi^2}{k^6} \int_0^\infty e^{-s} s^p ds \int_0^s u^r du \int_0^u \frac{t^q}{s^2 - t^2} dt$$

However,

$$\int_0^u \frac{t^q}{s^2 - t^2} dt = - \sum_{i=0}^{q/2-1} \frac{s^{2i}}{q-2i-1} [t^{q-2i-1}]^u + s^q \int_0^u \frac{dt}{s^2 - t^2}$$

$$= - \sum_{i=0}^{q/2-1} \frac{s^{2i} u^{q-2i-1}}{q-2i-1} + s^{q-1} \ln \left| \frac{s+u}{s-u} \right|$$

$$\begin{aligned} \int_0^s u^r du \int_0^u \frac{t^q}{s^2 - t^2} dt &= - \sum_{i=0}^{q/2-1} \frac{s^{2i}}{q-2i-1} \int_0^s u^{q+r-2i-1} du \\ &\quad + \frac{s^{q-1}}{2} \int_0^s u^r \ln \left| \frac{s+u}{s-u} \right| du \end{aligned}$$

$$= -s^{q+r} \sum_{i=0}^{q/2-1} \frac{1}{(q-2i-1)(q+r-2i)} + \frac{s^{q+r}}{2} \int_0^1 z^r \ln \left| \frac{1+z}{1-z} \right| dz$$

Hence,

$$\begin{aligned} C(p, q, r) &= \frac{2\pi^2}{k^6} \int_0^\infty s^{p+q+r} e^{-s} ds \left[- \sum_{i=0}^{q/2-1} \frac{1}{(q-2i-1)(q+r-2i)} \right. \\ &\quad \left. + \frac{1}{2} \int_0^1 z^r \ln \left| \frac{1+z}{1-z} \right| dz \right]. \end{aligned}$$

However, because the Hylleraas expansion is used, q is always an even integer and greater than zero, hence

$$\begin{aligned} - \sum_{i=0}^{q/2-1} \frac{1}{(q-2i-1)(q+r-2i)} &= - \sum_{j=0}^{q/2-1} \frac{1}{(2j+1)(2j+r+2)} \\ &= - \sum_{\substack{k=2 \\ k, \text{ even}}}^q \frac{1}{(k-1)(k+r)}. \end{aligned}$$

The logarithmic integral is treated in the following manner

$$\begin{aligned}
 D(r) &= \frac{1}{2} \int_0^1 z^r \ln \left| \frac{1+z}{1-z} \right| dz = \frac{1}{2} \int_0^1 z^r \ln(1+z) dz - \frac{1}{2} \int_0^1 z^r \ln(1-z) dz \\
 &= \frac{1}{2} \int_1^2 (x-1)^r \ln x \, dx - \frac{(-1)^r}{2} \int_0^1 (x-1)^r \ln x \, dx \\
 &= \frac{1}{2} \sum_{k=0}^r \binom{r}{k} (-1)^k \left[(-1)^r \int_1^2 x^k \ln x \, dx - \int_0^1 x^k \ln x \, dx \right] \\
 &= \frac{1}{2} \sum_{k=0}^r \binom{r}{k} (-1)^k \left\{ (-1)^r \left[\frac{x^{k+1}}{k+1} \ln x - \frac{x^{k+1}}{(k+1)^2} \right]_1^2 \right. \\
 &\quad \left. - \left[\frac{x^{k+1}}{k+1} \ln x - \frac{x^{k+1}}{(k+1)^2} \right]_0^1 \right\} \\
 &= \frac{1}{2} \sum_{k=0}^r \binom{r}{k} (-1)^k \left\{ (-1)^r \left[\frac{2^{k+1}}{k+1} \ln 2 - \frac{2^{k+1}}{(k+1)^2} + \frac{1}{(k+1)^2} \right] \right. \\
 &\quad \left. + \frac{1}{(k+1)^2} \right\} \\
 &= \frac{1}{2} \sum_{k=0}^r \binom{r}{k} \left\{ \frac{(-1)^k}{(k+1)^2} + \frac{(-1)^{r-k}}{k+1} \left[2^{k+1} \ln 2 - \frac{2^{k+1}}{k+1} + \frac{1}{k+1} \right] \right\}
 \end{aligned}$$

for $r \neq -1$, for the case $r = -1$, then

$$D(r) = D(-1) = \frac{\pi^2}{8}.$$

Thus, finally $C(p, q, r)$ may be written as

$$C(p, q, r) = \frac{2\pi^2 (p+q+r)!}{k^6} \left\{ - \sum_{\substack{k=2 \\ k \text{ even}}}^q \frac{1}{(k-1)(k+r)} + D(r) \right\} \quad (\text{IV.4})$$

All of the necessary integrals may now be evaluated in terms of these functions.

$$\langle \phi_0 | \chi_{1mn} \rangle = \left(\frac{8}{\pi}\right) N_{1mn} A(1, m, n+1) \left(\frac{2k}{k+4}\right)^{1+m+n+6} \quad (\text{IV.5})$$

where

$$N_{1mn} = \left[\frac{1}{A(1, m, n+1)} \right]^{\frac{1}{2}}$$

$\phi_0 = \frac{8}{\pi} e^{-2s/k}$ for the case of the ground state.

$$\langle \chi_{1mn} | r_{12}^p | \chi_{1'm'n'} \rangle = \frac{N_{1mn} N_{1'm'n'}}{k^p} A(L, M, N + p)$$

where $L = 1 + 1'$, $M = m + m'$ and $N = n + n' + 1$; two cases exist, $p = 0$ and $p = 1$.

For the He atom the Hamiltonian may be written as

$$\begin{aligned} H = & -k^2 \left[\frac{\partial^2}{\partial s^2} + \frac{\partial^2}{\partial t^2} + \frac{\partial^2}{\partial u^2} + \frac{2s(u^2 - t^2)}{u(s^2 - t^2)} \frac{\partial}{\partial s \partial u} + \frac{2t(s^2 - u^2)}{u(s^2 - t^2)} \frac{\partial}{\partial t \partial u} \right. \\ & \left. + \frac{4s}{s^2 - t^2} \frac{\partial}{\partial s} - \frac{4t}{s^2 - t^2} \frac{\partial}{\partial t} + \frac{2}{u} \frac{\partial}{\partial u} + \frac{4Zs}{k(s^2 - t^2)} \right] + \frac{k}{u} \end{aligned}$$

If the term in brackets is denoted as H' , then $-k^2 H' = H_0$ where H_0 is the unperturbed Hamiltonian. Making use of the following equations

$$\frac{\partial}{\partial s} x_{1mn} = \left(\frac{1}{s} - \frac{1}{2}\right) x_{1mn} \quad \frac{\partial^2}{\partial s^2} x_{1mn} = \left[\frac{1(1-1)}{s^2} - \frac{1}{s} + \frac{1}{4}\right] x_{1mn}$$

$$\frac{\partial}{\partial t} x_{1mn} = \frac{m}{t} x_{1mn} \quad \frac{\partial^2}{\partial t^2} x_{1mn} = \frac{m(m-1)}{t^2} x_{1mn}$$

$$\frac{\partial}{\partial u} x_{1mn} = \frac{n}{u} x_{1mn} \quad \frac{\partial^2}{\partial u^2} x_{1mn} = \frac{n(n+1)}{u^2} x_{1mn}$$

$$\frac{\partial^2}{\partial s \partial u} x_{1mn} = \left(\frac{1}{s} - \frac{1}{2}\right) \frac{n}{u} x_{1mn} \quad \frac{\partial^2}{\partial t \partial u} x_{1mn} = \frac{mn}{t} x_{1mn}$$

one may write

$$\begin{aligned} H|x_{1mn}\rangle &= [k^2 \left\{ \frac{1}{s} - \frac{1(1-1)}{s^2} - \frac{1}{4} - \frac{m(m-1)}{t^2} - \frac{n(n+1)}{u^2} \right. \\ &\quad + \frac{2}{s^2-t^2} \left[\left(\frac{n}{2} + 1 - \frac{2Z}{k}\right)s - (1-m)(n+2) + n1 \frac{t^2}{u^2} \right. \\ &\quad \left. \left. - \frac{n}{2} \frac{st^2}{u^2} - mn \frac{s^2}{u^2} \right] \right\} + \frac{k}{u}] x_{1mn} \\ &= k^2 x_{1mn} \{ 1[-1, 0, 0] - \frac{1}{4}[0, 0, 0] - 1(1-1)[-2, 0, 0] \\ &\quad - m(m-1)[0, -2, 0] - n(n+1)[0, 0, -2] + \frac{1}{k}[0, 0, -1] \\ &\quad + \frac{1}{s^2-t^2} \left[(n+2 - \frac{4Z}{k})[1, 0, 0] - 2(1-m)(n+2)[0, 0, 0] \right. \\ &\quad \left. + 2n1[0, 2, -2] - n[1, 2, -2] - 2mn[2, 0, -2] \right] \} \end{aligned}$$

where $[\alpha, \beta, \gamma] = s^\alpha t^\beta u^\gamma$.

One may now write

$$\begin{aligned}
 \langle x_{1mn} | r_{12} H_O | x_{1'm'n'} \rangle &= \frac{N_{1'm'n'} N_{1mn}}{k^5} \left\{ \sum_{i=1}^5 F_i(1', m', n') \right. \\
 &\times A(L + \alpha_i^F, M + \beta_i^F, N + \gamma_i^F + 1) + \sum_{i=1}^5 G_i(1', m', n') \\
 &\times B(L + \alpha_i^G, M + \beta_i^G, N + \gamma_i^G + 1) \left. \right\} \quad (IV.7)
 \end{aligned}$$

$$\begin{aligned}
 \langle x_{1mn} | H_O r_{12} | x_{1'm'n'} \rangle &= \frac{N_{1mn} N_{1'm'n'}}{k^5} \left\{ \sum_{i=1}^5 F_i(1', m', n' + 1) \right. \\
 &\times A(L + \alpha_i^F, M + \beta_i^F, N + \gamma_i^F + 1) + \sum_{i=1}^5 G_i(1', m', n' + 1) \\
 &\times B(L + \alpha_i^G, M + \beta_i^G, N + \gamma_i^G + 1) \left. \right\} \quad (IV.8)
 \end{aligned}$$

$$\begin{aligned}
 \langle x_{1mn} | H | x_{1'm'n'} \rangle &= \frac{N_{1mn} N_{1'm'n'}}{k^4} \left\{ \sum_{i=1}^6 F_i(1', m', n') \right. \\
 &\times A(L + \alpha_i^F, M + \beta_i^F, N + \gamma_i^F) + \sum_{i=1}^5 G_i(1'm'n') \\
 &\times B(L + \alpha_i^G, M + \beta_i^G, N + \gamma_i^G) \left. \right\} \quad (IV.9)
 \end{aligned}$$

$$\begin{aligned}
 \langle x_{1mn} | H_O r_{12} H_O | x_{1'm'n'} \rangle &= \frac{N_{1mn} N_{1'm'n'}}{k^3} \left\{ \sum_{i=1}^5 F_i(1', m', n'+1) \right. \\
 &\times \left[\sum_{j=1}^5 F_j(1', m', n'+1) A(L + \alpha_i^F + \alpha_j^F, M + \beta_i^F + \beta_j^F, N + \gamma_i^F + \gamma_j^F + 1) \right.
 \end{aligned}$$

$$\begin{aligned}
& + \sum_{i=1}^5 G_j(1', m', n'+1) B(L + \alpha_i^F + \alpha_j^G, M + \beta_i^F + \beta_j^G, N + \gamma_i^F + \gamma_j^G + 1)] \\
& + \sum_{i=1}^5 G_i(1', m', n'+1) [\sum_{j=1}^5 F_j(1', m', n'+1) B(L + \alpha_i^G + \alpha_j^F, \\
& M + \beta_i^G + \beta_j^F, N + \gamma_i^G + \gamma_j^F + 1) + \sum_{j=1}^5 G_j(1', m', n'+1) \\
& \times C(L + \alpha_i^G + \alpha_j^G, M + \beta_i^G + \beta_j^G, N + \gamma_i^G + \gamma_j^G + 1)] \} \quad (IV.10)
\end{aligned}$$

$$\begin{aligned}
\langle H_{\chi_{1mn}} | H_{\chi_{1', m', n'}} \rangle &= \frac{N_{1mn} N_{1', m', n'}}{k^2} \{ \sum_{i=1}^6 F_i(1, m, n) [\sum_{j=1}^6 F(1', m', n') \\
& \times A(L + \alpha_i^F + \alpha_j^F, M + \beta_i^F + \beta_j^F, N + \gamma_i^F + \gamma_j^F) + \sum_{j=1}^5 G_j(1', m', n') \\
& \times B(L + \alpha_i^F + \alpha_j^G, M + \beta_i^F + \beta_j^G, N + \gamma_i^F + \gamma_j^G)] + \sum_{i=1}^5 G_i(1, m, n) \\
& [\sum_{j=1}^6 F_j(1', m', n') B(L + \alpha_i^G + \alpha_j^F, M + \beta_i^G + \beta_j^F, N + \gamma_i^G + \gamma_j^F) \\
& + \sum_{j=1}^5 G_j(1', m', n') C(L + \alpha_i^G + \alpha_j^G, M + \beta_i^G + \beta_j^G, N + \gamma_i^G + \gamma_j^G)] \} \\
& \quad (IV.11)
\end{aligned}$$

where the above quantities α_i , β_i , γ_i , F_i and G_i are given in the table below. It should be noted that the value of the integral $\langle \chi_{\ell mn} | H_0 | \chi_{\ell' m' n'} \rangle$ is found by using Eq. (IV.9) but using the limit of the first summation as 5 rather than 6.

Table 12

<u>i</u>	<u>α_i^F</u>	<u>β_i^F</u>	<u>γ_i^F</u>	<u>$F_i(1mn)$</u>	<u>α_i^G</u>	<u>β_i^G</u>	<u>γ_i^G</u>	<u>$G_i(1mn)$</u>
1	0	0	0	$-\frac{1}{4}$	0	0	0	$-2(1-m)(n+2)$
2	-1	0	0	1	1	0	0	$(n+2 - 4Z/k)$
3	-2	0	0	$-1(1-1)$	0	2	-2	$21n$
4	0	-2	0	$-m(m-1)$	1	2	-2	$-n$
5	0	0	-2	$-n(n+1)$	2	0	-2	$-2mn$
6	0	0	-1	$1/k$				

With the expressions given above all the integrals needed for the two methods may be computed.

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